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DIFFUSIONAL AND KINETIC PHENOMENA ASSOCIATED WITH FOULING

CONSIDERATIONS ON THE EFFECT OF HYDRODYNAMIC AND THERMAL CONDITIONS

by

R. NIJSING

1964

Joint Nuclear Research Center
Ispra Establishment - Italy

Engineering Department - Heat Transfer

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CONTENTS

DIFFUSIONAL AND KINETIC PHENOMENA ASSOCIATED WITH FOULING - CONSIDERATIONS ON THE EFFECT OF HYDRODYNAMIC AND THERMAL CONDITIONS

I. INTRODUCTION

Fouling is a phenomenon known since many years in all fields of engineering dealing with flow of fluids. It is the deposition at the flow channel walls of matter originally present in the fluid. If heat is transported through these walls, such a deposit represents an additional thermal resistance and hence it may reduce the economy of the process.

In the design of heat transfer equipment fouling usually is accounted for by employing large safety factors and/or providing for simple means of system cleaning. This procedure is fully justified in conventional industrial processes since the costs of heat transfer equipment hardly ever appear to be a determining economic factor. In nuclear power generation systems the situation is entirely different. First in view of the high heat fluxes occurring, the thermal performance of the fuel element is very sensitive to the presence of a fouling layer. Second fouling may lead to local fuel element damage under conditions where the overall thermal performance of this element still is satisfactory. In the third place no simple means seem to exist for cleaning fuel element heating surfaces. In view of the above it is clear that necessarily measures have to be taken limiting fouling rates to a level which is acceptable from the point of view of economic reactor operation. Obviously this best can be done, if one disposes of a good understanding of the nature of the phenomena which give rise to fouling.

The fouling mechanisms in nuclear reactors can be expected to be directly associated with type of coolant and construction materials. The fouling processes dealt with in this report are related to organic cooled reactors. These reactors will be provided with a coolant circulating system of normal steel, whereas the coolant envisaged is a mixture of terphenyl isomers. In actual fact in the coolant also limited amounts will be present of side products (high boilers, low boilers and gases) which result from radiolysis and pyrolysis in the reactor. Furthermore there will be traces of various inorganic impurities which originate from corrosion processes in the coolant circulation system and also partly from the coolant fabrication process itself.

Experimental evidence obtained suggests that in organic coolants at least two basically different types of fouling may be distinguished [1, 2]. These fouling types will be referred to in this report as "molecular" fouling and "particle" fouling. "Molecular" fouling is thought to be due to rapid, diffusion controlled, thermal decomposition near the heating surface of soluble partly inorganic compounds. "Particle" fouling is believed to be associated with the presence in the coolant of particles (chiefly of inorganic nature) in the micron size range.

Also the limited thermal and radiolytic stability of the organic coolant compounds may to a considerable extent be responsible for fouling. At high temperature and under radiation, coolant decomposition occurs and at the same time high molecular weight products are being formed. In several experimental studies it has been observed that the latter compounds have a detrimental effect on fouling [3, 14].

Theoretical studies on fouling hitherto mainly were concerned with chemical and physico-chemical aspects of this process [4, 5]. Recently chemical techniques have been developed which may lead to substantial decreases in fouling rates [6]. The basic understanding of fouling however still leaves much to be desired. No theory exists sofar, explaining satisfactorily even in a qualitative manner, all experimental data available. It is thought that this situation can be noticeably improved by giving more attention to the effect of hydrodynamic and thermal conditions on diffusional and kinetic phenomena involved in fouling. The above consideration led to the theoretical study presented in this report.

The approach adopted here originates from a previous study, which dealt with diffusional phenomena in turbulent pipe flow [7]. The attempt has been made to separate as far as possible the effects on fouling due to physico-chemical factors from those related to the hydrodynamic and thermal conditions. In order to specify these conditions in mathematical terms, in Chapter 2, basic relationships have been presented pertaining to hydrodynamics and heat transfer in turbulent channel flow. In subsequent Chapters fouling mechanisms have been discussed and an attempt has been made to derive fouling rate expressions for various idealized mechanisms.

II. BACKGROUND INFORMATION ON HYDRODYNAMIC AND THERMAL CONDITIONS IN TURBULENT CHANNEL FLOW.

2.1. Hydrodynamic parameters in a uniform geometry.

The deposition of fouling products at the heating surface requires a transport of these products in the coolant normally to this surface; it further involves chemical decomposition processes close to the heating surface. Both types of processes are markedly influenced by hydrodynamic conditions. It hence is clear that a knowledge of these conditions is of great importance in a fundamental study on fouling.

For the present purpose the hydrodynamic conditions are sufficiently well characterized by the parameters enumerated below:

- the bulk coolant velocity,
- the velocity distribution in the region close to the wall,
- the thickness of the "viscous layer" near the wall,
- the average residence time of a fluid element in the viscous layer.

The expressions presented hereafter enable the above parameters to be evaluated for conditions of turbulent flow in a uniform*) channel geometry provided with smooth walls.

2.1.1. Bulk coolant velocity.

The bulk coolant velocity is given by the expression:

$$u_b = \frac{Q_v}{A} \qquad (2\text{-}1)$$

where Q_v is the volumetric flow rate and A is the flow section. The velocity u_b together her with channel diameter and kinematic viscosity of coolant determine the hydrodynamic conditions near the wall.

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*) Meant is a channel geometry characterized by a uniform shear stress distribution (e.g. a circular tube or an annular slit).

2.1.2. Velocity distribution in the region close to the wall.

Reliable velocity measurements in the region very close to the wall have been made by only a few investigators. The "average" velocity distribution, resulting from LAUFER's measurements in an isothermal turbulent flow [8], has been plotted in dimensionless form in figure 1.

Heat transfer from the wall to the coolant which leads to the existence of non-isothermal conditions near the wall will slightly distort this velocity distribution. The effect is however small enough to be ignored here.

Dimensionless velocity u^+ and wall distance y^+ are defined by the expressions:

$$u^+ = \frac{u_y}{\sqrt{\frac{\tau_w}{\rho}}} \qquad (2\text{-}2)$$

$$y^+ = \frac{y\sqrt{\frac{\tau_w}{\rho}}}{\nu} \qquad (2\text{-}3)$$

where:

y = wall distance, taken in a direction normally to the wall,

u_y = the "average" velocity at wall distance y,

τ_w = shear stress at the wall,

ν = kinematic viscosity of coolant,

ρ = coolant density.

The shear stress τ_w is given by:

$$\tau_w = 1/2 \; f \; \rho \; u_b^2 \qquad (2\text{-}4)$$

where in the range of Reynolds number 10^4-10^5 the friction factor f can be evaluated employing the Blasius expression:

$$f = 0.079\ Re^{-1/4} \qquad (2\text{-}5)$$

In terms of eqns (2-4) and (2-5) the expressions (2-2) and (2-3) can be rewritten as:

$$\frac{u_y}{u_b} = 0.2\ u^+\ Re^{-1/8} \qquad (2\text{-}6)$$

$$\frac{y}{d_{eq}} = 5\ y^+\ Re^{-7/8} \qquad (2\text{-}7)$$

where d_{eq} is the equivalent hydraulic diameter of the channel*).

Eqns (2-6) and (2-7) together with the dimensionless velocity distribution in fig. 1 enable the velocity distribution near the wall to be calculated for any Reynolds number lying between 10^4 and 10^5. An illustrative calculation has been carried out for geometrical and hydrodynamic conditions lying in the range envisaged for ORGEL, i.e.:

$$Re = 70.000$$

$$d_{eq} = 4.5\ mm$$

$$u_b = 6\ m/sec$$

The result is presented in figure 2.

2.1.3. The thickness of the "viscous layer" near the wall.

The existence of a "laminar sublayer" adjacent to the wall has been in the past a basic assumption underlying many theories on turbulent channel flow [9, 10, 11]. There is definite experimental evidence however, that at wall distances far smaller than the thickness of the "laminar sublayer" still important velocity fluctuations occur [8, 12, 13].

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*) Is defined by the ratio of 4 x flow section to wetted perimeter.

In a previous study [7] a model has been discussed describing the hydrodynamic behaviour of the fluid close to the wall. According to this model at the wall elementary viscous boundary layers grow by viscous momentum diffusion till a certain critical thickness; subsequently they then desintegrate again due to hydrodynamic instability. The latter process is accompanied by mixing with fluid distant from the wall.

The definition of the overage thickness of the elementary viscous boundary layers is arbitrary since:

- in boundary layers the velocity varies asymptotically with wall distance,
- for the conditions considered here, the influence of irregular turbulent motion on momentum transport becomes increasingly important with wall distance.

The experimental evidence available shows that for values of the dimensionless wall distance y^+ smaller than 10, the flow phenomena are influenced only to a minor extent by the turbulence of the main flow. The value of the dimensionless velocity corresponding to the above value of y^+ is according to figure 1 approximately 8.4.

The layer thickness y_{10} corresponding to $y^+ = 10$ can be calculated utilizing the eqn (2-7). For the geometrical and hydrodynamic conditions specified on page 8 one then finds

$$y_{10} = 1.3\ 10^{-2}\ \text{mm}$$

2.1.4. The average residence time of a fluid element in the "viscous layer".

The knowledge of residence times of fluid elements in the viscous region close to the wall can improve the understanding of chemical decomposition phenomena there.

According to ref. [7] one finds for the axial distance Δx_o over which elementary viscous boundary layers grow prior to turbulent breakdown:

$$\frac{\Delta x_o}{d_{eq}} = 1400\ (1/2\ f)^{-0.5}\ Re^{-1} \qquad (2\text{-}8)$$

Since breakdown of the elementary viscous boundary layer leads to mixing with neighbouring fluid, the average residence time of a fluid element in the viscous layer at a distance y from the wall will be

$$\frac{\Delta x_o}{u_y} .$$

For the geometrical and hydrodynamic conditions specified on page 8, residence time calculations have been made. The results are presented in table I.

TABLE 2-1

Residence time of fluid elements in the viscous boundary layer.

(Re = 70 000, d_{eq} = 4.5 mm, u_b = 6 m/sec).

dimensionless wall distance	dimensionless velocity	wall distance	velocity at wall distance y	residence time of fluid element in boundary layer
y^+	u^+	$\frac{y}{(\mu)}$	u_y (cm/sec)	$t = \frac{\Delta x_o}{u_y}$ (millisec)
0	0	0	0	∞
0.5	0.5	0.65	15	1.2
0.75	0.75	1	22	8.2
1	1	1.3	30	6
2	2	2.6	60	3
3	3	3.9	89	2
5	4.9	6.5	146	1.2
10	8.4	13	250	0.7
15	10.5	19.4	312	0.6

2.2. Thermal parameters in a uniform geometry.

Since fouling involves phenomena of thermal coolant decomposition a basic understanding of this process also requires a knowledge of the thermal conditions in the coolant. For the present purpose these thermal conditions are sufficiently well characterized by the following parameters:

- the bulk coolant temperature,
- the heating surface temperature,
- the temperature profile in the region close to the wall,
- the thickness of the thermal boundary layer.

Numerical evaluation of the above parameters, for conditions of turbulent flow through a uniform heating channel, can be carried out with the aid of the expressions presented herafter.

2.2.1. The bulk coolant temperature.

The bulk coolant temperature of a fluid flowing through a circular tube, uniformly heated around the periphery, is defined by the equation:

$$T_b = \frac{\int_o^R u_r \, T_r \, r \, dr}{\int_o^R u \, r \, d \, r} \qquad (2\text{-}9)$$

The frequent use of this kind of average coolant temperature is due to the fact that at any axial position x in the channel it can easily be evaluated from inlet coolant temperature and heat input utilizing the relation:

$$Q_x = (T_{b.x} - T_{b.in}) \, c_p \, \rho \, u_b \, A \qquad (2\text{-}10)$$

where Q_x = heat taken up by coolant at axial position x,

$T_{b.x}$ = bulk coolant temperature at axial position x,

$T_{b.in}$ = inlet bulk coolant temperature,

c_p = specific heat of coolant,

ρ = coolant density.

For organic coolants under conditions of turbulent flow the main resistance to heat transfer is localized near the heating surface (see 2.2.3.). Hence over the greatest part of the flow section the coolant temperature will vary little and lie close to the bulk temperature.

2.2.2. The heating surface temperature.

The heating surface temperature can be evaluated for a given local heat flux and bulk coolant temperature from the relation:

$$T_{(x)} = \frac{q_{(x)}}{\alpha_{(x)}} + T_{b.x} \qquad (2\text{-}11)$$

where $q_{(x)}$ is the heat flux at an axial position x in the channel and $\alpha_{(x)}$ is the heat transfer coefficient at that location.

For a coolant having a Prandtl number lying between 2 and 10 for flow conditions characterized by $10^4 < Re < 10^5$, the heat transfer coefficient is predicted by the dimensionless correlation

$$Nu = 0.0197\ Re^{0.82}\ Pr^{0.4} \qquad (2\text{-}12)$$

The above equations is a simplified form of a theoretical relationship presented in reference [7]. The heat transfer coefficients predicted by it exceed slightly those given by the conventional Dittus-Boelter relation.

For an illustrative calculation a coolant is considered having the following physical properties*):

specific heat	c_p	=	2350 J/kg °C
thermal conductivity	λ	=	0.114 W/m °C
kinematic viscosity	ν	=	$3.9\ 10^{-7}$ m^2/sec

*) These are the approximate physical properties at 350°C of a terphenyl mixture, manufactured by PROGIL (France) under the name OM_2, to which 15 % radiolytic high boilers have been added.

density ρ = 860 kg/m^3

Prandtl number Pr = 6.9

For the geometrical and hydrodynamic conditions specified on page 8 , one then finds, employing eqn (2-12), a heat transfer coefficient of 10^4 W/m^2 °C. For a heat flux of 1000 kW/m^2, then the difference between heating surface temperature and bulk coolant temperature is 100 °C. The heating surface temperature thus found for a bulk coolant temperature of 350 °C is 450 °C.

2.2.3. The temperature profile in the region close to the wall.

According to ref [7] the ratio between temperature drop in the viscous region and the difference between heating surface temperature and bulk coolant temperature, is given by

$$\frac{T_w - T_o}{T_w - T_b} = \frac{u_o^+ (1/2\,f)^{0.5}}{u_o^+ (1/2\,f)^{0.5} + \left(1 - u_o^+ (1/2\,f)^{0.5}\right) Pr^{-2/3}} \qquad (2\text{-}13)$$

where T_o is the temperature at the edge of the viscous region and where the dimensionless velocity $u_o^+ = 14.7$.

For a Reynolds number of 70 000 and a Prandtl number of 6.9, the above ratio becomes 0.91.

Employing a method similar to that outlined in ref [7] for the evaluation of a theoretical velocity profile near the wall one can derive the following expression for the temperature distribution close to the heating surface:

$$\frac{T_w - T_y}{T_w - T_o} = 0.068\, y^+ Pr^{1/3} - 0.00157\, y^{+2} Pr^{2/3} + 0.0000123\, y^{+3} \cdot Pr \qquad (2\text{-}14)$$

The above expression is valid for fluids with a Prandtl number larger than 1. It has no physical significance for values of the dimensionless variable y^+ larger than 55.

Employing eqns (2-13) and (2-14) the temperature distribution has been evaluated for the conditions given on pages 12 and 13. The result is graphically represented in fig. 3.

III. "MOLECULAR" FOULING.

3.1. Introductory remarks.

In the forced convection fouling experiments*) carried out by A. E. C. L. in Canada it has been found that the fouling deposits principally consist of crystalline inorganic material (mainly iron compounds) [1,2]. Furthermore in many of these experiments the following observations were made:

- The fouling layers contained more inorganic material than was initially present in the coolant.

- The rate of fouling increased with coolant velocity.

In view of the above experimental evidence, it was concluded that in the cold parts of the circulating system iron dissolves into the coolant**), e. g. through formation of soluble organic complex compounds. It was reasoned that such compounds decompose closely to the heating surface due to thermal instability and subsequently deposit at the surface. Experimental evidence obtained by Phillips Petroleum Company [14] is in support of the suggestion that inorganic materials like iron are to some extent "soluble" in the coolant.

It would be of great interest to examine whether the "molecular" fouling mechanism proposed is indeed consistent with the experimental evidence obtained by A. E. C. L. It is the main objective of the present considerations to do this. The next section is devoted to entirely theoretical considerations on mass transfer phenomena with simultaneous chemical reaction at the wall. In a subsequent section the theoretical relationships derived are employed for the evaluation of "molecular" fouling rates. The latter then are compared with those experimentally found by A. E. C. L.

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*) The experiments referred to here have been performed in circuits of normal steel and the coolant employed was a purified mixture of terphenyl isomers and OMRE high boilers, containing less then 5 ppm iron and less than 8 ppm ash.

**) The chemical nature of these compounds has not yet been established. It seems however certain that the solubility effect is closely associated with the presence of small amounts of chlorine in the coolant.

3.2. Mass transfer accompanied by chemical reaction in the thermal boundary layer.

3.2.1. Transfer mechanisms.

Relatively little fundamental knowledge exists on mass transfer in turbulent flow, arising due to a chemical reaction near the channel wall. In a recent theoretical study an analysis was given of mass transfer phenomena in the absence of a chemical reaction [7]. The basic concepts underlying this analysis are:

- Turbulent flow of a fluid past a smooth wall involves the continuous formation and breakdown of elementary viscous boundary layers adjacent to the wall*).

- Transfer of momentum, heat and mass in a growing elementary boundary layer takes place by molecular diffusion processes for which mathematical descriptions are available.

- The average axial length**) and thickness of an elementary boundary layer are characterized by dimensionless parameters which can be determined in a straight forward manner from experimental hydrodynamic data.

The above concepts proved to be consistent with a variety of phenomena observed in experiments which were related to fluid flow, heat- and mass transfer. Furthermore the analysis led, for conditions where the main resistance to transfer is situated near the wall, to transfer relationships which are in good agreement with data experimentally obtained.

The elementary viscous boundary layers are not attached to the wall but their position may be assumed to change rapidly and in a stastistical manner. In this connection it ought to be emphasized that althought transfer rates are steady, for steady macroscopic conditions, the actual mechanism closely to the wall is essentially one involving important time- and space variations of the "concentration" of the transferable quantity ***). In the case of heat transfer, heat is diffusing into the growing viscous boundary layer and the temperature pro-

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*) This model was already employed in Chapter 2 to evaluate residence times of fluid elements in the region close to the wall.

**) The average axial length of an elementary viscous boundary layer is given by eqn (2-8).

***) These types of variations have been experimentally demonstrated. [15].

file near the wall varies considerably with axial position in the boundary layer. In the case of mass transfer the same is true for concentration profiles.

The analysis referred to above can be extended to conditions where mass transfer is accompanied by a chemical reaction. The reaction considered here results from thermal instability of a reactant present in the fluid and it takes place in the high temperature region close to the heating surface.

3.2.2. Formulation and mathematical description of the problem.

The idealized process for which a physical and mathematical description is being sought can be summarized as follows:

- The fluid contains a certain amount of solute A which above a given "critical" temperature T_c, becomes unstable and decomposes*) into an insoluble compound B. The reaction is assumed to be irreversible, isothermal and of the first order.

- The fluid passes in turbulent flow a heating channel with the heating surface at a temperature T_w which exceeds the "critical" temperature T_c.

- The reaction product B crystallizes at the heating surface without forming particles in the solution**).

- The physical process, involving change of phase at the crystal interface is very rapid compared with the diffusion rate of reaction product towards the heating surface.

For the description of this process the viscous boundary layer growth model is employed. In the growing elementary viscous boundary layer the solute A is removed by reaction at wall distances where the

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*) For the mathematical description it is irrelevant whether this occurs by a rapid irreversible chemical reaction or by just exceeding the solubility limit of reactant A.

**) This is a known and frequently occurring phenomenon in crystallization processes. It arises from the facts that the solubility can be exceeded and that under certain circumstances crystal growth takes place preferentially to spontaneous nucleation and formation of particles.

temperature exceeds the value T_c. Suppletion of A to the reaction zone occurs by diffusion from the main body of the fluid. The reaction product B diffuses away from the reaction zone into the main flow as well as to the heating surface where it deposits. The above process, illustrated by schematic temperature and concentration profiles in fig. 4, is described by the following set of differential equations:

(velocity distribution) $$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \frac{\partial^2 u}{\partial y^2} \qquad (3\text{-}1)$$

(continuity) $$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \qquad (3\text{-}1\,a)$$

(temperature distribution) $$u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = a \frac{\partial^2 T}{\partial y^2} \qquad (3\text{-}2)$$

(concentration distribution of reactant) $$u \frac{\partial [A]}{\partial x} + v \frac{\partial [A]}{\partial y} = D_A \frac{\partial^2 [A]}{\partial y^2} - k_{r,t} [A]^{*)} \qquad (3\text{-}3)$$

(concentration distribution of reaction product) $$u \frac{\partial [B]}{\partial x} + v \frac{\partial [B]}{\partial y} = D_B \frac{\partial^2 [B]}{\partial y^2} + k_{r,t} [A]^{*)} \qquad (3\text{-}4)$$

The boundary conditions imposed are:

$x = o, \quad y \geqslant o; \quad u = u_o, \quad T = T_o, \quad [A] = [A]_o$

$y = 0, \quad x \geqslant 0; \quad u = v = o, \quad T = T_w, \quad [A] = o, \quad [B] = o$

$y = \infty, \quad x \geqslant o; \quad u = u_o, \quad T = T_o, \quad [A] = [A]_o, \quad [B] = o.$

If the temperature dependence of the reaction rate constant $k_{r,t}$ and the physical properties ν, a, D_A and D_B is known, theoretically all requirements for the solution of the above system of differential

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*) It is convenient to express the concentrations $[A]$ and $[B]$ in molar units ($kmol/m^3$).

equations are fulfilled. The mathematical procedure to be employed however is extremely complex. The problem therefore has been simplified by making the following additional assumptions:

- All physical properties are independent of temperature.
- The reaction is instantaneous at temperatures exceeding T_c.

In view of the latter assumption the reaction is taking place in a plane along the wall instead of in a zone and the eqns (3-3) and (3-4) are to be replaced by:

$$u \frac{\partial [A]}{\partial x} + v \frac{\partial [A]}{\partial y} = D_A \frac{\partial^2 [A]}{\partial y^2} \qquad (3\text{-}5)$$

$$u \frac{\partial [B]}{\partial x} + v \frac{\partial [B]}{\partial y} = D_B \frac{\partial^2 [B]}{\partial y^2} \qquad (3\text{-}6)$$

The above equations govern the transport of reactant and reaction product towards and away from the reaction plane respectively. An additional boundary condition becomes:

$$y = y_R, \quad x \geqslant 0, \quad T = T_c, \quad [A] = 0 \text{ and}$$

$$D_A \frac{\partial [A]}{\partial y} = D_B \frac{\partial [B]_1}{\partial y} - D_B \frac{\partial [B]_2}{\partial y} \quad *)$$

The new situation is schematically represented in fig. 5.

The reaction of solute A involves an interaction with the temperature field. Since the reaction was assumed to be isothermal it does not influence the temperature distribution in the boundary layer. Hence the latter can be obtained, independently of the reaction occurring, by solving eqns (3-1) and (3-2). An exact solution for this part of the problem has been presented by POHLHAUSEN [16]. An approximate,

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*) The term $D_B \frac{\partial [B]_1}{\partial y}$ refers to diffusion towards the wall and the term $- D_B \frac{\partial [B]_2}{\partial y}$ refers to diffusion towards the main-stream.

but much more simple method was originated by VON KARMAN [17] and described in detail by ECKERT [18]. In this method the boundary layer temperature distribution is approximated by a polynomial of four functions which are determined by solving the heat flow equation of the boundary layer. The result thus obtained well agrees with the exact solution in ref. [16]. The problem of mass diffusion (eqns 3-5 and 3-6) also can be solved in two different manners. An exact solution can be obtained, employing a method very similar to that indicated by FRIEDLANDER and LITT [19]. An approximative procedure, similar to that outlined by POTTER [20], was preferred here since it leads in a straight forward manner to relatively simple transfer relationships. Relevant calculations have been presented in Annex I. The results obtained can be summarized as follows:

- 1) If $D_A = D_B$, the average deposition rate of reaction product B at the wall during the growth of an elementary viscous boundary layer is independent of the value of T_c, provided the latter is larger than T_o. It is given by:

$$q_m = 0.664\, M_B\, [A]_o\, D_A^{2/3}\, \nu^{-1/6}\, \left(\frac{u_o}{\Delta x_o}\right)^{1/2} \qquad (3\text{-}7)$$

where M_B is the molecular weight of B.

- 2) If $T_w = T_c$, the average deposition rate of B at the wall during the growth of an elementary viscous boundary layer is independent of the value of D_B and also given by eqn (3-7).

- 3) For conditions where $D_A \neq D_B$ and $T_w > T_c$, the average deposition rate of B at the wall during the growth of an elementary viscous boundary layer is

$$q_m = 0.664\, M_B\, [B]_{o,f}\, D_B^{2/3}\, \nu^{-1/6}\, \left(\frac{u_o}{\Delta x_o}\right)^{1/2} \qquad (3\text{-}8)$$

where $[B]_{o,f}$ is given by the approximate expression (a-27).

- 4) The average conversion rate of solute A is: (3-9)

$$q_m = 0.664\, M_A \left([A]_o + [A]_{w,f}\right) D_A^{2/3}\, \nu^{-1/6}\, \left(\frac{u_o}{\Delta x_o}\right)^{1/2}$$

where $[A]_o + [A]_{w.f}$ is given by the approximate expression (a-23).

The equations (3-7), (3-8) and (3-9) hold for transfer in growing boundary layers. The values of the diffusivities D_A and D_B are so small, that the whole resistance against transfer is situated in the boundary layer. Hence the above equations can be transformed into relationships holding for turbulent flow by substitution of the parameters u_o and Δx_o. The velocity u_o can be expressed in terms of a dimensionless velocity u_o^+ (see eqn 2-2):

$$u_o = u_o^+ \left(\frac{\tau_w}{\rho}\right)^{0.5} = u_o^+ (1/2\, f)^{0.5} \cdot u_b \qquad (3\text{-}10)$$

where according to ref [7] $u_o^+ = 14.7$. The parameter Δx_o is given by eqn (2-8). Eqns (3-7), (3-8) and (3-9) now become respectively

$$q_m = 0.0136\, M_B \cdot [A]_o \cdot \frac{D_A}{d_{eq}} Re^{0.875} Sc^{1/3} \qquad (3\text{-}11)$$

$$q_m = 0.0136\, M_B \cdot [B]_{o.f} \frac{D_B}{d_{eq}} Re^{0.875} Sc^{1/3} \qquad (3\text{-}12)$$

$$q_m = 0.0136\, M_A \left([A]_o + [A]_{w.f}\right) \frac{D_A}{d} Re^{0.875} Sc^{1/3} \qquad (3\text{-}13)$$

In these equations the Schmidt number Sc represents the ratio of kinematic viscosity ν and diffusivity D.

The above theoretical expressions give rise to the following remarks:

- Equation (3-11) is identical to the equation for entirely diffusion controlled mass transfer presented in ref [7].

- According to expressions (3-11) and (3-12) the rate of molecular fouling increases with coolant velocity, in line with the Canadian observations [1, 2].

- The expressions (3-11), (3-12) and (3-13) have been derived for the assumption of an infinitely fast reaction. In actual fact the reaction rate constant has a finite value. Dimensional considerations show that the transfer rates will lie closer to

the predictions of the above equations the greater the value of dimensionless group $\frac{k_r \Delta x_o}{u_o}$ *). In terms of turbulent flow parameters this group can also be written as: $\frac{k_r}{f. \nu u_b^2}$.

- High values of the reaction product concentration $[B]_R$ in the reaction zone are likely to entail the formation of colloidal particles. Since the diffusivity associated with such particles is significantly smaller than that of the molecular compounds, the occurrence of this process will, at least in a first stage **), reduce fouling rates. In this connection it is worth pointing out that according to Annex I, the maximum concentration $[B]_R$ increases with $\frac{T_w - T_c}{T_w - T_o}$. It hence would not be entirely unexpectable if for the type of fouling here considered, a rise of wall temperature led to a decrease in fouling rate.

3.3. Calculation of "molecular" fouling rates.

For simplicity it is assumed that the diffusivities D_A and D_B are equal. Hence for the calculation of theoretical fouling rates only the relationship (3-11) needs to be employed.

It is supposed that the diffusivity D_A is associated with a complex compound made up of terphenyl and iron. Lacking any experimental information on the structure and molecular weight of such a compound, the diffusivity D_A will be evaluated for a terphenyl molecule. The correlation employed for this purpose is the semiempiempirical relationship of WILKE and CHANG [21]:

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*) Here k_r is arbitrarily defined as the value of the reaction rate constant at the centre of the reaction zone.

**) If such particles are not removed by means of a purification system and the bulk fluid remains saturated with regard to the solute A, high concentrations of colloidal matter ultimately build up in the system which may markedly affect fouling.

$$D_A = 7.4\ 10^{-8}\ \frac{(X\ M_S)^{0.5}\ T}{\mu_s\ V_A^{0.6}} \qquad (3\text{-}14)$$

Here:

M_S = molecular weight of solvent (in grams),

T = absolute temperature (in ^oK),

μ_s = dynamic viscosity of solvent (in centipoises),

V_A = molecular volume of solute at normal boiling point (in $cm^3/gmol$),

X = association parameter for solvent.

Experiments reported in ref [14] provide support for the assumption that iron (the solute A) is slightly soluble in terphenyl mixtures. At temperatures around 300 ^oC The saturation concentration seems to have a value around 0.5 p.p.m. From A.E.C.L. fouling experiments it appears that an iron content decrease in the order of 1 ppm, due to Attapulgus clay coolant purification, gave rise to a marked decrease in fouling rate. This suggests that the concentration in the coolant of a "harmful" iron compound is of the same order of magnitude. In the present calculations an iron saturation concentration of 0,0004 kg/m^3 will be employed *). This corresponds to an iron content of 0.5 ppm.

The fouling rate will be evaluated for conditions which at A.E.C.L. led to a fouling rate of 109 μgrams/cm^2 hour. These conditions are summarized below:

hydraulic diameter of heating channel	d_{eq}	1.2 cm
bulk coolant velocity	u_b	7 m/sec
Reynolds number	Re	140.000
bulk coolant temperature	T_b	357 ^oC
heating surface temp.	T_w	476 ^oC

*) The product $M_B [A]_o$ thus has this value.

In the calculation of theoretical "molecular" fouling rates, employing the relationship (3-11), the diffusivity D_A and the Schmidt number Sc are evaluated at coolant temperature of 400°C. At this temperature the coolant employed by A.E.C.L. (Santowax OM + 30 % OMRE high boilers) has a dynamic viscosity of approximately $3.6\ 10^{-4}$ kg/msec (= 0.36 cp), a density of 820 kg/m^3 and a kinematic viscosity of approximately $0.45\ 10^{-6}$ m^2/sec. For the following values of the parameters in the eqn (3-14):

$$X = 1$$
$$M_s = 230$$
$$T = 673$$
$$\mu_s = 0.36$$
$$V_A = 266$$

the diffusivity D_A becomes $7.2\ 10^{-9}$ m^2/sec. In view of the value of the kinematic viscosity given above, the Schmidt number Sc becomes 63.

Use of the relationship (3-11) then leads to a "molecular" fouling rate, i.e. to an iron deposition rate, of $49.5\ 10^{-8}$ kg/m^2 sec. This is equivalent to a fouling rate of 180 μgrams/cm^2 hour.

In view of the uncertainties in the estimated values of the saturation concentration $M_B\ [A]_o$ and the diffusivity D_A and taking into account the simplifying assumptions on the basis of which eqn (3-11) was derived, the agreement between the theoretical fouling rate of 180 μgrams/cm^2 hour and that experimentally found of 109 μgrams/cm^2 hour must be considered to be good. It was already noted on page 20 that the positive influence of an increase in coolant velocity on fouling rate, observed by A.E.C.L., also is predicted by eqn(3-11). At given hydrodynamic and thermal conditions, deposition rates for this type of fouling will increase in a linear fashion with the concentration of the "harmful" thermally unstable iron compound. On page 21 it was however already observed that decomposition of this compound is likely to entail the formation of colloidal particles. The next Chapter will deal with calculations on fouling, due to the presence of particles.

IV. "PARTICLE" FOULING.

4.1. General

The formation of fouling layers at the wall made up of solid particles originally present in the coolant is due to a process in which the following steps may be distinguished:

- formation of particles,
- growth of particles,
- transport of particles to the wall,
- adhesion of particles to the wall.

For a good understanding of this type of fouling indicated here as "particle" fouling,it is necessary to dispose of a fundamental knowledge of each of the above step processes. In the present considerations the main attention is fixed on the processes of particle transport to the wall and their adhesion there. It is not the purpose to discuss in detail the mechanism of the other step processes; only a few aspects of these processes which bear a direct relationship to particle transport will be briefly referred to.

Very small particles suspended in fluid media are subject to an incessant and irregular movement, the so-called Brownian movement which is a direct consequence of molecular motion. It is possible to describe the macroscopic kinetic behaviour of large groups of identical particles in terms of a diffusion coefficient*). Since the diffusion coefficient associated with these particles is fairly small, the main resistance to particle transport in turbulent flow lies in the flow region close to the wall. Consequently this particle transport process can be described employing a model which is very similar to that outlined in the preceding Chapter. This leads us again to considerations on diffusion phenomena in the elementary viscous boundary layer. The next section is devoted to this. In a subsequent section the transport equations derived are transformed into relationships holding for turbulent flow. A criterion for the adhesion of particles at the wall is also given. Finally the effect of β current on particle deposition rate is discussed.

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*) If the particle size distribution is not uniform, but known a certain number of diffusion coefficients associated with particles of the same size has to be employed in a mathematical description of "Brownian" particle transport.

4.2. Particle diffusion in the elementary viscous boundary layer.

The assumptions underlying the present physical description of diffusive particle transport in a growing viscous boundary layer can be summarized as follows:

- The conditions in the fluid near the wall are isothermal.
- The physical properties of the fluid are not affected by the presence of particles.
- All particles are identical and for the mathematical treatment they are regarded as infinitely small.
- The rate of particle adhesion at the wall is proportional to the particle concentration there. In the terminology of chemical kinetics one then may write:

$$R = k_p \, c_w \qquad (4\text{-}1)$$

where R = the particle adhesion rate at the wall (kg/m^2 sec),
c_w = the particle concentration at the wall (kg/m^3),
k_p = the particle adhesion rate constant (m/sec).

The process of particle diffusion in the growing viscous boundary layer is illustrated by the schematic particle concentration profiles given in figure 6. In mathematical terms this process can be formulated as follows:

(momentum) $$u \frac{\partial u}{\partial y} + v \frac{\partial u}{\partial x} = \nu \frac{\partial^2 u}{\partial y^2} \qquad (3\text{-}1)$$

(continuity) $$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \qquad (3\text{-}1a)$$

(particle diffusion) $$u \frac{\partial c}{\partial y} + v \frac{\partial c}{\partial x} = D_p \frac{\partial^2 c}{\partial y^2} \qquad (4\text{-}2)$$

The boundary conditions imposed on the above equations are:

$$y = 0, \quad x \geqslant 0 \qquad u = 0, \quad D_p \frac{\partial c}{\partial y} = k_p c_w$$

$$y = \infty, \quad x \geqslant 0 \qquad u = u_o, \quad c = c_o$$

$$x \leqslant 0, \quad y \geqslant 0 \qquad u = u_o, \quad c = c_o$$

Here c_o is the particle concentration in the main stream.

A general mathematical solution of eqns (3-1), (3-1a) and (4-2) for the above boundary conditions is not yet available. It can immediately be seen however that for two extreme cases the problem is considerably simplified.

- If the adhesion rate constant k_p has a very low value the particle concentration distribution near the wall is uniform and the rate of particle deposition at the wall is given by

$$q_p = k_p \cdot c_o \qquad (4-3)$$

Under these circumstances the particle deposition rate is entirely determined by the kinetics of the adhesion process.

- For a very high value of the adhesion rate constant the particle concentration near the wall is close to zero and particle deposition becomes entirely diffusion controlled. Solution of the eqns (3-1), (3-1a) and (4-2) then leads to the familiar type of expression for the average particle deposition rate in the growing viscous boundary layer [16]:

$$q_p = 0.664\, c_o\, D_p^{2/3}\, \nu^{-1/6} \left(\frac{u_o}{\Delta x_o}\right)^{1/2} \qquad (4-4)$$

An estimation of the adhesion rate constant k_p, for which the particle deposition rate is a certain but relatively small percentage lower than the limiting rate given by eqn (4-4), can be made in a simple manner. A deposition rate b % lower than the limiting rate according to eqn (4-4) is due to a decrease in the average diffusion driving force of approximately b % (see also fig. 6). This means that a particle concentration is established at the wall which has the approximate average value:

$$c_w = \frac{b}{100} c_o \qquad (4\text{-}5)$$

The average rate of adhesion has to be equal to the average rate of suppletion by diffusion:

$$R = k_p c_w = 0.664 \frac{100 - b}{100} c_o D_p^{2/3} \cdot \nu^{-1/6} \left(\frac{u_o}{\Delta x_o}\right)^{1/2} \qquad (4\text{-}6)$$

In view of eqns (4-5) and (4-6) one thus directly obtains:

$$k_p = 0.664 \frac{100 - b}{b} D_p^{2/3} \nu^{-1/6} \left(\frac{u_o}{\Delta x_o}\right)^{1/2} \qquad (4\text{-}7)$$

4.3. Diffusion controlled particle deposition in turbulent channel flow.

The equation (4-3) also holds for particle deposition in turbulent channel flow, since it does not contain any hydrodynamic parameters. The eqns (4-4) and (4-7) can be transformed into expressions valid for turbulent flow conditions, by substituting the parameters u_o and Δx_o in a manner similar to that outlined in 3.2.2. One then obtains for the limiting "particle" fouling rate:

$$q_p = 0.0136 c_o \frac{D_p}{d_{eq}} Re^{0.875} Sc^{1/3} \qquad (4\text{-}8)$$

The value of k_p, for which the "particle" fouling rate is a small percentage b lower than the above limiting rate is:

$$k_p = 0.0136 \frac{100 - b}{b} \frac{D_p}{d_{eq}} Re^{0.875} Sc^{1/3} \qquad (4\text{-}9)$$

The limiting "particle" fouling rate relationship (4-8) shows a great similarity with the expressions for "molecular" fouling developed in the preceding Chapter. Also here an increase in velocity has a positive effect on the rate of fouling. According to eqn (4-9) the adhesion rate constant k_p for which the process still is diffusion controlled increases in an almost linear fashion with bulk fluid velocity.

It is of interest to point out here that entirely diffusion controlled particle deposition not necessarily means that all particles impingent on the wall remain attached to it. This is made clear by calcula-

tions presented in Annex II. E. g. for the following conditions:

Channel diameter	d_{eq}	=	4.5 mm
Reynolds number	Re	=	70 000
Diffusivity of particle	D_p	=	$2.73\ 10^{-11}$ m^2/sec
Kinematic viscosity of fluid	ν	=	$3.9\ 10^{-7}$ m^2/sec *)

Particle deposition rate is 95 % of limiting rate according to eqn (4-8);

it was found that only 3.5 percent of the particles contacting the wall adhere to it.

The evaluation of "particle" fouling rates for given hydrodynamic conditions, according to eqn (4-8) requires the knowledge of D_p. For a suspension containing small spherical particles of uniform size, the particle diffusivity is according to EINSTEIN [28].

$$D_p = \frac{k\ T_k}{3\ \pi\ \mu\ d_p} \qquad (4\text{-}10)$$

where:

k = the Boltzmann constant ($1.38\ 10^{-23}$ J/°K),

T = the temperature (°K)

d_p = particle diameter

Employing the eqns (4-8) and (4-10) for certain conditions fouling rates have been calculated. The results, brought together in table 4-1, give rise to a series of observations which have been summarized hereafter.

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*) This is the kinematic viscosity of OM_2, containing 15 % HB at a temperature of 350 °C.

TABLE 4-1

Limiting "particle" fouling rates for various particle diameters.

Conditions	particle diameter (μ)	"particle" fouling rate (μg/cm^2 hr)
Channel diameter d_{eq} = 4.5 mm		
Bulk fluid velocity u_b = 6 m/sec	0.01	115.6
	0.02	73.
	0.05	39.7
Bulk fluid temperature T_b = 350 °C	0.03	29.
	0.1	25
Kinematic viscosity of fluid ν = 3.9 10^{-7} m^2/sec	*)	
	0.5	8.6
Fluid density ρ = 860 kg/m^3	*)	
	1	5.4
Particle concentration c_o = 0.002 kg/m^3 (i.e. 2.3 ppm)	*)	
	2	3.4
	*)	
	5	1.8

*) As is shown in this Chapter, the assumption of infinitely small particle size, here entails too low values of the limiting particle fouling rate.

- It appears that for a given particle concentration, the limiting "particle" fouling rate appreciably increases with a decrease in particle size.

- The "particle" fouling rate evaluated for very small particles (0.01μ) is of the same order of magnitude as the "molecular" fouling rate calculated in the preceding Chapter. Since both, "particle" fouling and "molecular" fouling, show the same dependence on flow conditions, it cannot be established with certainty from experiments which of the two mechanisms actually predominates. The crystalline character of the fouling deposits observed in the A. E. C. L. experiments [2] at first sight points to a "molecular" type fouling mechanism. Recently it has been shown however that also colloidal particles can give rise to the formation of crystalline deposits [22, 23].

- The fouling rates evaluated are of the same order of magnitude as those found in many of the out of pile experiments carried out by A. E-C. L. for about the same coolant velocity*) and for an iron content comparable to the particle concentration c_o employed. It ought to be acknowledged however that the particle size is not known for these experiments.

- In the calculations, the influence of heating surface temperature has been disregarded. It was supposed that non-isothermal conditions near the wall only affect particle deposition rate, by their influence on the physical properties of the fluid and hence on the particle diffusivity. For most cases the resulting increase in particle deposition rate is not great.

- Eqn (4-8) has been developed for the simplifying assumption that the particles are infinitely small. For particles having a finite size diffusion controlled particle deposition will be faster than predicted by eqn (4-8), since the distance to be travelled by a particle before contacting the wall is diminished by half a particle diameter. The data presented in table (4-1) hence are somewhat too low and as is easily seen the error involved increases with particle diameter. In order to establish at which particle diameter this error becomes important it is proposed to calculate particle concentration profiles (for infinitely small particles) and to determine subsequently which percentage of the total concentration variation occurs over a wall distance equal to half the particle diameter. The actual limiting particle deposition rate then will be roughly the same percentage higher than that predicted by eqn (4-8). The theoretical concentration distribution for infinitely small

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*) The magnitude of the channel diameter in the A. E. C. L. experiments differs by a factor 3 from that used in the calculations. According to eqn (4-8) this does not affect significantly the fouling rate however.

particles is given by the expression:

$$\frac{c}{c_o} = 0.068\, y^{+\,1/3}\, Sc^{1/3} - 0.00157\, y^{+\,2}\, Sc^{2/3} + 0.0000123\, y^{+\,3}\, Sc \qquad (4\text{-}11)$$

which can be derived in exactly the same manner as eqn (2-14). Employing the hydrodynamic conditions specified in table (4-1), concentration distributions have been evaluated for various particle diameters. The results are graphically represented in figure 7. It is seen that for diameters larger than 0.5 μ, the positive effect of particle size on deposition rate amounts to more than 70 %.

Particle size also has a large influence on the process of adhesion. A discussion related to this is presented in the next section.

4.4. Considerations on particle adhesion.

A particle impingent on the wall adheres to it if the attractive force existing between the wall and the particle exceeds the drag force exerted by the fluid on the particle. The above criterion can be expressed quantitatively if relationships for both forces are available.

Little is known regarding the physical mechanism which gives rise to the attractive force between a particle and a solid boundary. According to KRUPP et al. [24] the origin of adhesion must be sought in the molecular VAN DER WAALS forces. A theory for evaluating these forces however does not yet exist. The actual force involved in particle adhesion further also depends on the area of contact between particle and solid boundary. It therefore will be strongly dependent on mechanical properties, like surface geometry and visco-elastic behaviour, of both the solid boundary and the particle. In practice therefore adhesive forces have to be determined experimentally. The only useful information available is due to experiments performed by BOEHME et al. [25]. These investigators measured the adhesive forces between spherical particles (2 μ and 4 μ diameter) of iron and iron oxide respectively and solid boundaries of iron and iron oxide respectively. In line with the expectations the adhesive forces measured for a smooth surface geometry exceed by far those measured for a wrinkled surface geometry. For adhesion to a smooth solid boundary of 2 μ diameter particles, characterized by a wrinkled surface geometry,

it was found that 60 % *) of the particles adhere with forces greater than $1.4\ 10^{-8}$ Newton. Since furthermore the adhesive force was observed to be roughly proportional to the particle diameter one may state in a more general manner that for a particle diameter of mμ 60 % of the particles adhere with a force greater than $0.7\ m\ 10^{-8}$ Newton. Lacking other information this force will be used in subsequent calculations on particle adhesion, as the adhesive force.

It is assumed that the particles are spherical and that they are small with respect to the thickness of the viscous region. The drag force on a particle in contact with a perfectly smooth wall then can be approximated using the expression:

$$F_{dr} = 1/8\ f_s\ \pi\ d_p^2\ \rho\ u_a^2 \qquad (4\text{-}12)$$

where f_s is the friction factor for flow around a sphere and u_a is the average fluid velocity at a wall distance equal to half the particle diameter.

For values of $\frac{d_p\ u_a}{\nu} < 2$ the friction factor is given by:

$$f_s = \frac{24\ \nu}{d_p\ u_a} \qquad (4\text{-}13)$$

and for $2 < \frac{d_p\ u_a}{\nu} < 500$, one has [26]:

$$f_s = 18.5 \left(\frac{\nu}{d_p\ u_a}\right)^{0.6} \qquad (4\text{-}14)$$

In connection with the calculation method here proposed it ought to be remarked:

- that the expressions (4-12), (4-13) and (4-14) are valid for free flow around a sphere, whereas here the "sphere" is in contact with the wall and the average velocity varies in a linear fashion with wall distance,

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*) Since particles are not identical and even for one particle surface properties can vary considerably around the periphery, one may not expect that the attractive force is the same for each collision of a particle with the wall.

- that the important velocity fluctuations occurring up to very small wall distances have been ignored.

Hence it is to be expected that the actual hydrodynamic forces acting on a particle tending to adhere at the wall are somewhat higher than those calculated here.

Employing the same hydrodynamic conditions as those specified in table 4-1, calculations have been made of drag forces and adhesive forces for various particle diameters. The results have been collected in table (4-2).

Taking into account that the drag forces calculated are slightly too high, one may expect on the basis of the data in table 4-2, that anyway for a particle size below 0.5 micron the adhesive forces*) exceed the drag forces. For the hydrodynamic conditions here considered, such particles thus have a great probability of adhering to the wall after having come into contact with it. Hence it may be expected that under those conditions "particle" fouling is diffusion controlled.

4.5. Qualitative remarks on effects within the core of a nuclear reactor.

The fouling mechanisms discussed in the preceding sections pertain to conventional conditions. Within the core of a nuclear reactor additional mechanisms may be responsible for fouling. It is worth noting at the outset that relevant experimental evidence available is not conclusive. Atomics International reports that within the reactor core the fouling process is more rapid than in out of pile experiments [27], where as the experimental results obtained by A.E.C.L. [1, 2] do not indicate a significant effect. It may well be however that the above controversy is only apparent and has its origin in the different experimental conditions employed.

It has been suggested [24, 4], that the electric current originating from the fuel and its cladding (β current) may influence the process of "particle" fouling. Due to this current an electric field is set up in the coolant near the cladding surface and particles present in the coolant are electrically charged. As a consequence electrostatic forces

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*) It is estimated that the adhesive forces, measured for rigid materials, which have been employed in the present calculations will not be smaller for particles present in an organic coolant, since the latter particles are provided with a "visco-elastic" coat of organic matter.

TABLE 4-2

Drag forces and adhesive forces on particles in contact with the wall.

Conditions	particle diameter (μ)	Reynolds number ($\frac{d_p u_a}{\nu}$)	Drag force (Newton)	Adhesive force (Newton)
channel diameter : d_{eq} = 4.5 mm	10	29	1.08 10^{-9}	70 10^{-9}
bulk fluid velocity : u_b = 6 m/sec	5	7.3	15.4 "	35 "
kinematic viscosity of fluid : ν = 3.9 10^{-7} m^2/sec	2	1.2	1.45 "	14 "
fluid density : ρ = 860 kg/m^3	1	0.29	0.36 "	7 "
	0.5	0.07	0.09 "	3.5 "
	0.1	0.003	0.0036 "	0.35 "
	0.08	$<$ 0.002	0.0023 "	0.56 "
	0.05	$<$ 0.002	0.0009 "	0.35 "

direct these particles to the cladding surface and tend to retain them there.

The rate of lateral particle transport due to the electrostatic force in the coolant primarily depends on the electric resistivity of the coolant. The magnitude of the electrostatic force on a particle at the surface of the fouling layer, on the other hand, is critically dependent on the electric resistivity of this layer. The relative importance of the above two effects also will depend on the value of the purely physical adhesive force (see 4.4.) and of the diffusive particle transport rate. It is obvious for instance that an increase in the adhesive force at the surface of a fouling layer due to electrostatic effects will not entail an acceleration of fouling, if this process is anyhow diffusion controlled.

It is stated by PARKINS [27, 4] that the electric resistivity of the organic coolant is so small that the resulting electrostatic force is not great enough to have an important effect on particle transport. The electric resistivity of the fouling layer however is considered sufficiently high to give rise to a significant electrostatic adhesive force. According to PARKINS the latter effect may, within the core of nuclear reactors, greatly contribute to "particle" fouling.

LANZA and VAN RUTTEN [5] pointed out that the electric resistivities of the fouling layer actually measured are by far too low to justify PARKINS' theory. Calculations were carried out by the same investigators to evaluate the velocity of iron particles towards the fuel cladding under the influence of the electrostatic force in the coolant. For conditions typical for the operation of an organic cooled reactor (UC fuel, neutron flux $2\ 10^{13}$ n/sec · cm^2, organic coolant having a viscosity of $2.2\ 10^{-4}$ kg/m sec) and for the assumption that the electrical resistivity is only slightly lower than that of the pure coolant it then was found that the lateral velocity of a particle having a diameter of about half a micron has the order of magnitude of 10 μ/sec.

The question may be raised which is the relative contribution to "particle" fouling due to the existence of this lateral particle transport, if it may be assumed that each particle impingent on the wall remainsattached to it. It is obvious that only the particles in the viscous region which are relatively close to the wall have a chance to be deposited there. The thickness of the flow region y_{de} depleted by the convective transport mechanism can be easily estimated. It is equal to the product of the lateral particle velocity and a time interval. In view of the facts:

- that the average velocity profile near the wall is linear

- that the lateral particle velocity is constant.

- that the centre of a particle contacting the wall is at a distance of 1/2 d_p from the latter,

it can easily be seen that this time interval is equal to the residence time, in the viscous boundary layer, of a fluid element situated in the centre of the flow region confined by planes at wall distances of 1/2 d_p and y_{de} respectively.

The hydrodynamic conditions considered here are those given on page 8. From table 2-1 in which residence times of fluid elements in the viscous boundary layer have been specified, it then results that the thickness of the depleted flow region y_{de} only amounts to a few tenths of a micron for a lateral particle velocity of 10 μ/sec. From the curve for $d_p = 0.5\,\mu$ in figure 7 it appears that for the same hydrodynamic conditions depletion due to diffusive particle transport is more important than that due to the convective transport mechanism considered here *).

4.6. Concluding remarks.

A previous attempt to describe the transport and subsequent deposition of particles has been reported by PARKINS [27, 4]. To calculate the flux of particles incident on the wall, non stationary diffusion of particles through a stagnant fluid layer was considered. The boundary conditions, adopted in the mathematical description, involved the assumptions that the fluid layer is infinitely thick and that all particles coming into contact with the wall are deposited there. It is known that the mathematical solution to this problem predicts the deposition rate to vary inversely with the square root of a time parameter [7]. The magnitude of the time parameter employed by PARKINS was the residence time of a fluid element in an "undisturbed laminar" layer near the wall. By comparing the theoretical predictions with fouling rates actually measured, the probability was evaluated that a particle remains attached to the wall after having come into contact with it (the socalled "sticking probability").

The following objections may be brought up against PARKINS' approach:

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*) A more sophisticated solution of the problem posed here should involve the solution of the basic boundary layer diffusion equation (4-2) in which a term representative for convective particle transport is inserted.

- In performing the calculations no account has been taken of the fluid behaviour close to the wall. Especially the estimation of the fluid element residence time in the zone near the wall is quite unrealistic.

- The theoretical relationship derived is only valid for the conditions of entirely diffusion controlled transfer. In making comparisons with experimental results no attention is being given to this restrictive condition.

- No distinction is being made between entirely different quantities like flux of particles incident on the wall and the collision frequency between particles and wall.

It is believed that the theoretical model developed in this Chapter presents a more realistic description of the "particle" fouling process. The adhesion criterion and the qualitative considerations on the β -current effect indicate that for conditions specific for an organic cooled reactor of the ORGEL type the particle deposition process is likely to be diffusion controlled for a particle size smaller than 0.5 micron. It is recognized that also this model has its limitations. E.g. it only allows fouling rates to be predicted for a known particle concentration and a known particle size distribution. Further the relationships developed are only valid for geometries provided with smooth walls. In this connection it is to be noted that large particles which cannot be deposited at a smooth surface in view of the high hydrodynamic drag forces there, are likely to be preferentially retained by surface protrusions and artificial roughnesses.

The theory developed does not predict that the rate of "particle" fouling to a heated wall is different from that to an unheated wall. Experimental evidence however shows that the formation of stable, adherent fouling layers preferentially occurs on the heating surface. The formation of such layers probably is positively influenced by the occurrence of chemical processes which bond the particles to each other and to the wall. Obviously these processes predominantly take place at the heating walls (pyrolytic reactions and within a nuclear reactor also radiolytic reactions). In view of their complexity and also since they do not affect the rate of particle deposition these processes will not be further discussed here. It only be remarked that the formation of stable fouling layers will not take place on surfaces where sufficiently strong chemical bonds cannot be established. Initial particle deposition on such surfaces will result into the formation of particle clusters which are washed off by the flowing coolant once they have become so large that the drag forces exceed the adhesive forces.

An important result from the theoretical considerations presented is that the rather controversial experimental evidence regarding the effect of coolant velocity on "particle fouling" can be readily explained. For particles below a certain size where the deposition process is diffusion controlled, an increase in coolant velocity will enhance fouling. On the other hand for particles above a certain size where the deposition process is also partly controlled by adhesion, an increase in coolant velocity leads to a decrease in the adhesion rate constant and hence to a reduction in fouling rate. It thus may be concluded that it primarily depends on the particle size distribution whether the effect of coolant velocity on fouling is positive or negative.

Since "particle fouling" is critically dependent on size distribution and concentration of the particles it obviously also depends on all those parameters and processes which affect the size distribution and concentration. The exact chemical constitution of the coolant, the coolant temperature and the type of coolant purification process employed may be expected to be factors of prime importance. It does not lie within the scope of this report to examine these factors here. Only a few specific effects associated with the "organic" constitution of the coolant will be discussed. The effects referred to are related to the influence of hydrodynamic and thermal conditions on coolant decomposition. The following Chapter is devoted to this discussion.

V. EFFECTS ASSOCIATED WITH THE LIMITED CHEMICAL STABILITY OF THE ORGANIC COOLANT.

5.1. General

In preceding Chapters processes were discussed which were primarily due to the presence in the coolant of inorganic impurities. The organic compounds of the coolant however are also directly involved in fouling since they decompose at high temperature and under conditions of radiation. These decomposition processes lead to the formation of a great variety of products both of high and low molecular weight. It has been observed that the products of high molecular weight can greatly enhance fouling. [3].

The present considerations deal with effects which entail the formation of fouling layers mainly consisting of organic matter. It is believed that high molecular weight products will precipitate on minor solid impurities already present in the coolant and thus lead to the formation of principally organic particles. The deposition of these particles at the walls then takes place by mechanisms already described in the preceding Chapter. Further it is likely that under certain conditions also the pyrolytic decomposition processes in the high temperature region near the heating surface may contribute substantially to the formation of organic fouling layers. The complexity of the phenomena involved does not allow a rigorous description of these processes. The objective therefore rather is to present a qualitative picture which improves the understanding of these processes and which may eventually be employed as a guideline for basic experimental studies.

In the next section a method is described for evaluating pyrolytic decomposition effects. A subsequent section of this Chapter deals with speculative considerations regarding the effect of hydrodynamic and thermal conditions on the formation of organic fouling layers.

5.2. Pyrolysis in the thermal boundary layer

In Chapter 2 it was shown that for organic coolants the greatest part of the temperature difference between heating surface and coolant is situated in the thermal boundary layer. Since chemical reaction rates sharply rise with temperature, pyrolytic decomposition will be most rapid in this region. The present purpose is to evaluate quantitatively these decomposition effects.

From table 2-1 in Chapter 2 it appears that the average residence time of fluid elements in the viscous region is relatively short even at distances very close to the wall. Hence if the pyrolytic decomposition is not excessively fast at the temperature of the heating surface, the change in coolant decomposition of a fluid element, during its residence time in the viscous region, still will be relatively small. Under these conditions it is justified to relate decomposition rates at any position in the thermal boundary layer to a coolant having the bulk composition. The pyrolytic coolant decomposition rate in the thermal boundary layer then can be evaluated using the approximative procedure summarized below:

- the average temperature distribution in the thermal boundary layer is calculated for a given bulk temperature with the aid of the expressions (2-13) and (2-14);

- employing this temperature distribution, the coolant decomposition rate in a volume element $z.x.\Delta y$ *) can be found, employing reaction rate data available from pyrolytic capsule experiments;

- for a given bulk coolant temperature, the pyrolytic decomposition rate in the thermal boundary layer then is obtained by integrating the contributions due to the volume elements $z.x.\Delta y$ over the thickness of the thermal boundary layer;

- if an appreciable axial bulk coolant temperature gradient exists it is necessary to consider volume elements $z.\Delta x.\Delta y$ and to integrate subsequently over the channel length x as well.

As an illustrative example the pyrolytic decomposition of the terphenyl mixture OM_2 has been calculated for the geometrical, hydrodynamic and thermal conditions specified on pages 8, 12 and 13. The chemical reaction data utilized are those enumerated in table 5-1.

It then appears that the coolant decomposition rate per unit of channel length in the thermal boundary layer is $2.6\ 10^{-7}$ kg/m hr, whereas that in the turbulent main flow is $6.8\ 10^{-7}$ kg/m hr. For the conditions employed here coolant pyrolysis in the thermal boundary layer thus is relatively unimportant . Notwithstanding this, pyrolytic decomposition effects in the thermal boundary layer may have a harmful effect on fouling. Discussions in this connection are presented in the next section.

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*) z is the periphery of the heating wall, x its axial length and Δy is an incremental wall distance.

TABLE 5-1

Pyrolytic decomposition rates*)

Temperature (°C)	Weight % decomposed per hour (%/hr)
350	0.004
360	0.006
370	0.009
380	0.016
390	0.03
400	0.05
410	0.09
420	0.16
430	0.3
440	0.5
450	0.9

*) Approximate values, based on pyrolytic decomposition data of Santowax OM + 27 % H B [30].

5.3. Speculative considerations on mechanisms involved in the formation of organic fouling layers.

After a sufficient residence time of the virgin coolant in a nuclear reactor or in a conventional heating system, significant amounts of high boilers (for a great part terphenyl dimers) have been formed. Pyrolytic decomposition of these high molecular weight products is known to be much more rapid at high temperatures than that of the terphenyls. Consequently the conditions near the heating surface will be relatively more important in determining high boiler decomposition.

Due to the combined effects of radiolysis and pyrolysis the high boiler decomposition leads to the formation of resinous products of very high molecular weight*) which are characterized by a still lower thermal stability. One may imagine that once the concentration of these "critical" high molecular weight compounds is sufficiently high, two types of processes may occur either of which favours the formation of organic fouling layers. A brief description of these processes is given below.

a) "Critical" high molecular weight products rapidly decompose in the thermal boundary layer under formation of insoluble reaction products which directly deposit at the heating surface. In this connection it is worth pointing out that for the conditions specified in table 2-1, the fluid elements at wall distances smaller than 0.1 μ, are at a temperature close to that of the heating surface for times larger than 7 msec. If the heating surface temperature is sufficiently high to cause an important formation of solid reaction products during such an interval, colloidal particles may be formed which partly deposit at the wall and partly diffuse into the main flow. Obviously the above process is closely related to the chemical kinetics of pyrolysis and to the diffusion characteristics of the harmful reaction products. The pyrolytic reactions are manyfold, possibly subject to catalytic effects and they vary in a complex manner with temperature. Furthermore the exact nature of the harmful reaction products is not known and likely to be critically dependent on the experimental conditions. In view of this there is little hope to evaluate formation rates of organic fouling layers, otherwise than by specifically directed experiments. Nevertheless the above remarks may prove to be useful in as far as they enable a physical interpretation of the effects of hydrodynamic and thermal conditions on "organic" fouling.

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*) The average molecular weight of the OMRE high boilers is approximately 500; compounds however have been identified in this mixture having molecular weights up to 3000 [29]. Notice that the molecular weight of a terphenyl is 230.

b) Another process, likely to be more important is due to the precipitation of high molecular weight compounds on minor solid impurities in the coolant. Since the solubility of these compounds diminishes with decreasing temperature this process will predominantly occur in the fully turbulent region of the flow and in parts of the coolant piping system where the temperature is lowest.*) Particles principally consisting of organic matter are thus being formed. The basic mechanisms by which these particles are deposited at the wall have been extensively discussed in the preceding Chapter.

One cannot theoretically predict the rate of formation of organic fouling layers for given hydrodynamic and thermal conditions. It is possible however to present a qualitative picture concerning the effect which the latter conditions have on "organic" fouling.

For a given geometrical configuration the most important variable affecting the hydrodynamic conditions is the bulk coolant velocity. A decrease in coolant velocity, the temperatures of heating surface and of coolant being kept constant, entails a growth in thickness of both the hydrodynamic and thermal boundary layers. As a consequence of this:

- The formation rate of "critical" high molecular weight compounds due to pyrolytic processes in the thermal boundary layer increases and hence the formation rate of "organic" particles also increases.

- The mechanical flow forces tending to prevent relatively coarse particles from adhering at the wall become smaller. Hence the probability that these particles deposit increases.

- For particles below a certain size where the deposition process is diffusion controlled, the deposition rate decreases in line with the predictions of eqn (4-8).

Obviously from the above one cannot conclude whether for a given experiment a decrease in coolant velocity has a positive or a negative effect on "organic" fouling. If in a fouling experiment a virgin coolant of pure terphenyl isomers is circulated in an initially clean circuit which is not provided with a coolant purification system, one may expect that fouling will be more rapid for low coolant velocities. Under those conditions all products likely to deposit at the wall have to be produced by chemical decomposition of the coolant. According as

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*) It thus may be expected that in a heated circulation system processes occurring outside the test section, may significantly influence fouling in the test section.

these products build up with time in the coolant, the rate of fouling increases*). After a sufficiently long time interval the total fouling rate will equal the formation rate of harmful decomposition products. Since the latter was shown to increase with a decrease in coolant velocity, this also will hold for the fouling rate. In case a purification system is being used which automatically removes all coarse particulate impurities and which maintains the concentration of the submicron particles at a constant level, a decrease in coolant velocity will entail a reduction in fouling**). This is due to the fact that the deposition of the submicron particles is diffusion controlled.

A main thermal variable is the heating surface temperature. In Chapter 2 it has been outlined in which manner it varies with flow conditions for a given heat flux and a given bulk coolant temperature. The direct effect of an increase in heating surface temperature is:

- More rapid pyrolytic decomposition in the thermal boundary layer and hence an increased formation rate of critical high molecular weight products. As a consequence fouling will be enhanced.

- A relatively small increase of "particle" diffusivity in the zone close to the heating surface due to the rise in coolant temperature there. The resultant increase in rate of "particle" fouling, in case this process is diffusion controlled, can be calculated employing eqns (4-8) and (4-10).

It is evident therefore that a rise in heating surface temperature causes an increase in fouling rate. It is worth noting however that this increase will be highest again if no coolant purification system is being employed. In case a purification system maintains the particle concentration and size at a constant level, the increase in fouling rate will be largely due to the temperature dependence of the "particle" diffusivity. For a terphenyl coolant one then may calculate that a rise in heating surface temperature of 10° C corresponds to an increase in fouling rate of approximately 5 %.

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*) In actual fact the impurities which are being formed also still have a catalytic effect on coolant decomposition and hence lead to an additional increase in fouling rate [29]

**) The above qualitative considerations show how sensitive experimental fouling results will be with regard to the experimental procedure adopted.

VI. FINAL CONSIDERATIONS.

In this report physical and mathematical descriptions have been presented of two types of fouling processes. In one process, designated as "molecular" fouling, the impurities giving rise to fouling are soluble and stable at the bulk coolant temperature whereas near the heating surface they decompose into products which deposit there. In the other process fouling is due to the presence in the coolant of solid impurities (particles). It has been shown that particles incident on the wall will adhere there, provided they are sufficiently small. Under those conditions the particle deposition is diffusion controlled.

Since the processes here referred to, involve diffusion controlled mass transport, they are similar as to the effect of hydrodynamic conditions. According to the theoretical predictions for both processes the fouling rate increases in an almost linear fashion with coolant velocity. For a given impurity level in the coolant an increase in heating surface temperature has little effect either on "molecular" fouling or on "particle" fouling. The slight increase predicted, is due to the temperature dependence of the diffusivity. The most significant difference between "molecular" fouling and "particle" fouling is that for a given impurity level the former takes place much more rapidly than the latter. Very small quantities of "unstable" soluble impurities therefore may already have a very harmful effect on fouling. A conclusion pertaining to "particle" fouling is that the rate of this process markedly increases with a decrease in particle size. Conditions which favour the coagulation of particles hence will lead to a reduction in fouling. As to the effect of in pile conditions on "particle " fouling it was shown that such an effect, if existing, will be critically dependent on the flow conditions and on the particle size.

Fouling will be markedly influenced by factors which favour the formation of harmful soluble impurities and of particles. These factors, being of chemical and physico-chemical nature, are partly unknown and hardly controllable. As a consequence they cannot be taken into account in a mathematical description of fouling. Theoretical predictions on fouling rates therefore only can be given if type, concentration and diffusion characteristics of the impurities present are known. Notwithstanding these difficulties, it appeared possible to calculate, on the basis of estimated impurity diffusivities, "molecular" fouling rates which reasonably well agree with those experimentally found by A. E. C. L. Qualitative remarks also have been presented on chemical effects associated with the use of an organic coolant. A detailed discussion of these effects however was considered to lie beyond the scope of this report.

The fouling rate expressions presented have been derived for a uniform geometry (e.g. circular tube) uniformly heated around the periphery and provided with smooth walls. In principle it is also possible to apply the theoretical relations to a more complex geometry with important heat flux variations around its periphery . This requires the knowledge of local flow and heat transfer conditions. A case of interest e.g. is cluster fuel element with closely spaced rods. The fact that such a fuel element is highly different from the uniform geometry and that the heat source distribution over its cross section may considerably vary has the following consequences:

- around the periphery of a fuel rod, important variations may occur of coolant velocity, coolant temperature and cladding surface temperature,

- flow and temperature conditions will be different for the various subchannels in the fuel element.

Hence one may expect that in certain locations of the fuel element, conditions will be particularly severe with regard to fouling. A method is actually being developed, enabling the local variations in flow and heat transfer to be theoretically evaluated. The theoretical expressions then can be used to predict local fouling rates in the fuel element. It further will be possible to employ results experimentally obtained in uniform geometries for local fouling predictions in the fuel element.

It ought to be emphasized that the above remarks apply to the case of single phase heat transfer. If nucleate boiling occurs (which may accidentally take place near the outlet of the fuel element), an entirely different situation may arise. In a cluster fuel element, boiling will initiate in the narrow flow region between two rods. The increase in flow resistance accompanying boiling then will lead to a flow redistribution and to a reduction in coolant velocity in the narrow regions. Due to this the local coolant temperature there will rise and the boiling process will become more vigorous. Although lateral turbulent interaction with neighbouring coolant of lower temperature partly counterbalances this effect, the equilibrium conditions established may be such as to promote locally rapid pyrolytic fouling. Once the latter process has initiated, it will become autocatalytic and result into a slow local burnout within the fuel element.

In view of the complexity of the fouling problem it is of the utmost importance to reduce as far as possible the extent of the experimental program required to solve this problem. It is believed that the present analysis may substantially contribute to this, by providing a guideline for the performance of basic experimental studies. It lies beyond the scope of this report to outline here an experimental program.

It seems worth pointing out however that a basic experimental research on fouling requires the use of methods which enable the coolant impurities to be characterized. As to the presence of solid impurities this implies that methods have to be developed enabling the particle concentration and the particle size distribution to be determined.

ANNEX I

MASS TRANSFER WITH INSTANTANEOUS CHEMICAL REACTION IN THE BOUNDARY LAYER.

At a temperature T_c lying between the wall temperature T_w and the temperature at the edge of boundary layer T_o the solute A reacts instantaneously and irreversibly under formation of a compound B which directly crystallizes at the wall.

Due to this reaction the following mass transport processes take place:

- Diffusion of solute A from the main stream where its concentration is $[A]_o$, to the reaction plane where its concentration is o.
- Diffusion of reaction product B from the reaction plane where its concentration has the maximum value $[B]_R$ to the wall where its concentration is o.
- Diffusion of reaction product B from the reaction plane to the main stream where its concentration is o.

The main purpose is to evaluate the deposition rate of reaction product B at the wall, i.e. its rate of diffusion to the wall and to find the conversion rate of solute A, i.e. its rate of diffusion to the reaction plane.

The reaction plane obviously is situated at a wall distance y_R. for which $T = T_c$. This wall distance can be evaluated for any axial position x in the boundary layer employing the approximate boundary layer temperature profile:

$$\frac{T_w - T}{T_w - T_o} = 3/2 \left(\frac{y}{\delta_{th}}\right) - 1/2 \left(\frac{y}{\delta_{th}}\right)^3 \qquad (a\text{-}1)$$

where δ_{th} is the "thermal" boundary layer thickness given by

$$\delta_{th} = 4.64 \left(\frac{\nu x}{u_o}\right)^{1/2} \cdot \left(\frac{\nu}{a}\right)^{-1/3} \qquad (a\text{-}2)$$

The concentration profiles of the compounds A and B are given by equations very similar to eqn (a-1). These equations however are expressed in terms of a diffusion boundary layer thickness δ_m defined

by:

$$\delta_m = 4.64 \left(\frac{\nu x}{u_o}\right)^{1/2} \left(\frac{\nu}{D}\right)^{-1/3} \qquad (a\text{-}3)$$

In fig. 5 schematic temperature and concentration profiles have been given for the case where $a > D_A > D_B$, the reaction taking place at a wall distance $< \delta_{m.B}$. Adopting POTTER's approach [20] fictitious wall concentrations $[A]_{w.f}$, $[B]_{w.f}$ and a fictitious main stream concentration $[B]_{o.f}$ have been introduced. In terms of these fictitious concentrations the concentration profiles in the boundary layer of the solute A and the reaction product B respectively become:

(diffusion towards reaction plane)

$$\frac{-[A]_{w.f} - [A]}{-[A]_{w.f} - [A]_o} = 3/2 \frac{y}{\delta_{m.A}} - \frac{1}{2} \left(\frac{y}{\delta_{m.A}}\right)^3 \qquad (a\text{-}4)$$

(diffusion towards wall, profile 1)

$$\frac{0 - [B]}{0 - [B]_{o.f}} = 3/2 \frac{y}{\delta_{m.B}} - \frac{1}{2} \left(\frac{y}{\delta_{m.B}}\right)^3 \qquad (a\text{-}5)$$

(diffusion towards main stream, profile 2)

$$\frac{[B]_{w.f} - [B]}{[B]_{w.f} - 0} = 3/2 \frac{y}{\delta_{m.B}} - \frac{1}{2} \left(\frac{y}{\delta_{m.B}}\right)^3 \qquad (a\text{-}6)$$

It is convenient to write $\frac{y_R}{th} = Z$, $\frac{\delta_{th}}{\delta_{m.A}} = R_1$ and $\frac{\delta_{th}}{\delta_{m.B}} = R_2$. In view of eqns (a-2) and (a-3) then:

$$R_1 = \left(\frac{a}{D_A}\right)^{1/3} \qquad (a\text{-}7)$$

$$R_2 = \left(\frac{a}{D_B}\right)^{1/3} \qquad (a\text{-}8)$$

If the values of T_w, T_c and T_o are such that $\frac{T_w - T_c}{T_w - T_o}$ is equal to m with $0 < m < 1$, then according to eqn (a-1) at $y = y_R$, one has:

$$m = 3/2\ Z - 1/2\ Z^3 \qquad (a\text{-}9)$$

Only such small values of m are regarded in the present considerations that y_R is smaller than both $\delta_{m.B}$ and $\delta_{m.A}$.

For $y = y_R$, the eqns (a-4), (a-5) and (a-6) can be rewritten as:

$$\frac{[A]_{w.f}}{[A]_{w.f} + [A]_o} = 3/2\ R_1\ Z - 1/2\ R_1^3\ Z^3 \qquad (a\text{-}10)$$

$$\frac{[B]_R}{[B]_{o.f}} = 3/2\ R_2\ Z - 1/2\ R_2^3\ Z^3 \qquad (a\text{-}11)$$

$$\frac{[B]_{w.f} - [B]_R}{[B]_{w.f}} = 3/2\ R_2\ Z - 1/2\ R_2^3\ Z^3 \qquad (a\text{-}12)$$

The condition that at the reaction plane the rate of suppletion of solute A has to be equal to the rate of diffusion of reaction product away from the reaction plane leads to:

$$D_A \frac{[A]}{y_{(y = y_R)}} = D_B \frac{\partial [B]}{\partial y_{(y = y_R)}} - D_B \frac{\partial [B]}{\partial y_{(y = y_R)}} \qquad (a\text{-}13)$$

(profile 1) (profile 2)

In view of eqns (a-4), (a-5), (a-6), (a-7) and (a-8) this equation can be further transformed to

$$\frac{[A]_o + [A]_{w.f}}{[B]_{w.f} + [B]_{o.f}} \left(\frac{1 - R_1^2 \, Z^2}{1 - R_2^2 \, Z^2} \right) = \left(\frac{D_B}{D_A} \right)^{2/3} \qquad (a\text{-}14)$$

In a boundary layer process involving diffusion controlled transfer of a compound C from the main stream, where it has a concentration $[C]_o$, towards the wall where the concentration is $[C]_w$, then the average rate of suppletion towards the wall is given by [16]:

$$\frac{q_m}{M_c} = 0.664 \left([C]_o - [C]_w \right) D_c^{2/3} \, \nu^{-1/6} \left(\frac{u_o}{\Delta x_o} \right)^{1/2} \qquad (a\text{-}15)$$

where M_c is the molecular weight of the substance C.

Hence the average deposition rate of reaction product B at the wall is given by

$$\frac{q_m}{M_B} = 0.664 \, [B]_{o.f} \, D_B^{2/3} \, \nu^{-1/6} \left(\frac{u_o}{\Delta x_o} \right)^{1/2} \qquad (a\text{-}16)$$

and the average conversion rate of solute A is expressed by

$$\frac{q_m}{M_A} = 0.664 \left([A]_o + [A]_{w.f} \right) D_A^{2/3} \, \nu^{-1/6} \left(\frac{u_o}{\Delta x_o} \right)^{1/2} \qquad (a\text{-}17)$$

The equations (a-16) and (a-17) contain the unknown concentrations $[B]_{o.f}$ and $[A]_{w.f}$ which can be determined, with the aid of the equations (a-9), (a-10), (a-11), (a-12) and (a-14).

As far as the evaluation of $[B]_{o.f}$ is concerned it is convenient to consider first the simple case for which $D_A = D_B$. Then, according to eqn (a-14):

$$[A]_o + [A]_{w.f} = [B]_{w.f} + [B]_{o.f} \qquad (a\text{-}18)$$

From eqns (a-10), (a-11) and (a-12):

$$\frac{[A]_{w.f}}{[A]_{w.f} - [A]_o} = \frac{[B]_{w.f}}{[B]_{w.f} + [B]_{o.f}} \qquad \text{(a-19)}$$

From eqns (a-18) and (a-19) then the important conclusion is obtained that

$$[B]_{o.f} = [A]_o \qquad \text{(a-20)}$$

This means that for $D_A = D_B$, the rate of deposition at the wall of the reaction product B is independent of the value of the temperature T_c, provided the latter is larger than T_o.

The value of $[A]_o + [A]_{w.f}$ can be determined in a simple manner from eqns (a-9), (a-10) and (a-7). For relatively small values of m, e.g. $m < 0.3$, the term $1/2\ Z^3$ in eqn (a-9) can be neglected and

$$Z \approx 2/3\ m \qquad \text{(a-21)}$$

Eqn (a-10) then can be written as

$$\frac{[A]_{w.f}}{[A]_{w.f} + [A]_o} = m R_1 - 8/54\ m^3 R_1^3 \qquad \text{(a-22)}$$

and this equation can be further developed to give:

$$[A]_{w.f} + [A]_o = \frac{[A]_o}{1 - m R_1 + 8/54\ m^3 R_1} \qquad \text{(a-23)}$$

For known values of the diffusivities a and D_A, R_1 is also known from eqn (a-7).

An approximative expression relating $[B]_{o.f}$ to $[A]_o$, for the case where $D_A \neq D_B$ can be obtained in the following manner. According to eqn (a-14) approximately

$$\frac{[A]_o + [A]_{w.f}}{[B]_{w.f} + [B]_{o.f}} = \left(\frac{D_B}{D_A}\right)^{2/3} \qquad \text{(a-24)}$$

Further in view of eqns (a-10), (a-11) and (a-12) one also approximately has:

$$\frac{[B]_{w.f}}{[A]_{w.f}} = \frac{D_A}{D_B} \qquad \text{(a-25)}$$

Eqns (a-24) and (a-25) then give:

$$[B]_{o.f} = [A]_o + [A]_{w.f}\left(\frac{D_A}{D_B}\right)^{2/3} - A_{w.f}\,\frac{D_A}{D_B} \qquad \text{(a-26)}$$

The latter equation, can in view of eqns (a-22) and (a-23) be further developed to

$$[B]_{o.f} = \frac{[A]_o}{1 - m R_1 + 8/54\, m^3 R_1^3}\left(\frac{D_A}{D_B}\right)^{2/3} + \\ - [A]_o\,\frac{m R_1 - 8/54\, m^3 R_1^3}{1 - m R_1 + 8/54\, m^3 R_1^3} \qquad \text{(a-27)}$$

It is worth noting that when $A_{w.f}$ is small with respect to $[A]_o$ i.e. if T_c has a value close to T_w, eqn (a-26) reduces to:

$$[B]_{o.f} = [A]_o\left(\frac{D_A}{D_B}\right)^{2/3} \qquad \text{(a-28)}$$

According to eqn (a-16) the deposition rate of reaction product B then becomes:

$$\frac{q_m}{M_B} = 0.664 \, [A]_o \, D_A^{2/3} \, \nu^{-1/6} \left(\frac{u_o}{\Delta x_o} \right)^{1/2} \qquad \text{(a-29)}$$

The reaction plane then coincides with the wall and the deposition rate is entirely controlled by diffusion of solute A to the wall.

ANNEX II

THE PROBABILITY OF PARTICLE ADHESION IN DIFFUSION CONTROLLED "PARTICLE" FOULING.

Diffusion controlled particle deposition not necessarily implies that all particles incident on the wall adhere to it. To show this the particle collision rate has to be compared with the particle deposition rate.

The procedure adopted to calculate the particle collision rate is the same as that employed in the kinetic theory of gases to calculate molecular collision frequencies. If the following simplifying assumptions are made:

- conditions of thermal equilibrium prevail,
- all particles have the same mass and may be considered as infinitely small,
- the particle motion is entirely chaotic and is not influenced by a net transport towards the wall,

the number of particles striking the wall per unit time and per unit area may be written as [31]:

$$\phi_{coll} = 1/4 \; n_w \sqrt{\frac{k \; T}{\pi \; m}} \qquad (b\text{-}1)$$

where n_w is the number of particles per unit of coolant volume close to the wall.and m is the mass of a particle.

In order to determine which percentage of the particles contacting the wall adhere to it, eqn (b-1) has to be compared to the expression:

$$q_p = 0.0136 \; \frac{100 - b}{100} \; c_o \; \frac{D_p}{d_{eq}} \; Re^{0.875} \; Sc^{1/3} \qquad (b\text{-}2)$$

Arbitrarily b is chosen to be 5. This means that the particle deposition rate is 95 % of the limiting deposition rate predicted by eqn (4-8). In that case the particle concentration at the wall n_w has a value which amounts to 5 % of the particle concentration in the bulk coolant.

An illustrative calculation has been carried out for the following conditions:

channel diameter	d_{eq}	=	4.5 mm
Reynolds number	Re	=	70 000
coolant temperature	T_b	=	350 °C (623 °K)
coolant density	ρ	=	860 kg/m^3
kinematic viscosity of coolant	ν	=	3.9 10^{-7} m^2/sec
particle diameter	d_p	=	0.1 μ
particle density	ρ_p	=	7.5 10^3 kg/m^3

According to eqn (b-2) the particle deposition rate in kg/m^2 sec then is

$$q_p = 3.3\ 10^{-5}\ c_o \qquad \text{(b-3)}$$

The number of particles adhering to the wall per unit time and per unit area then becomes:

$$\Phi_{adh} = 3.3\ 10^{-5}\ n_o \quad (m^{-2}\ sec^{-1}) \qquad \text{(b-4)}$$

Since $n_w = 0.05\ n_o$, eqn (b-1) predicts a particle collision rate

$$\Phi_{coll} = 9.4\ 10^{-4}\ n_o \quad (m^{-2}\ sec^{-1}) \qquad \text{(b-5)}$$

From eqns (b-4) and (b-5) it then results that for a particle deposition rate which is 95 % diffusion controlled and for the conditions here considered 1 of 28 particle collisionswith the wall leads to particle adhesion.

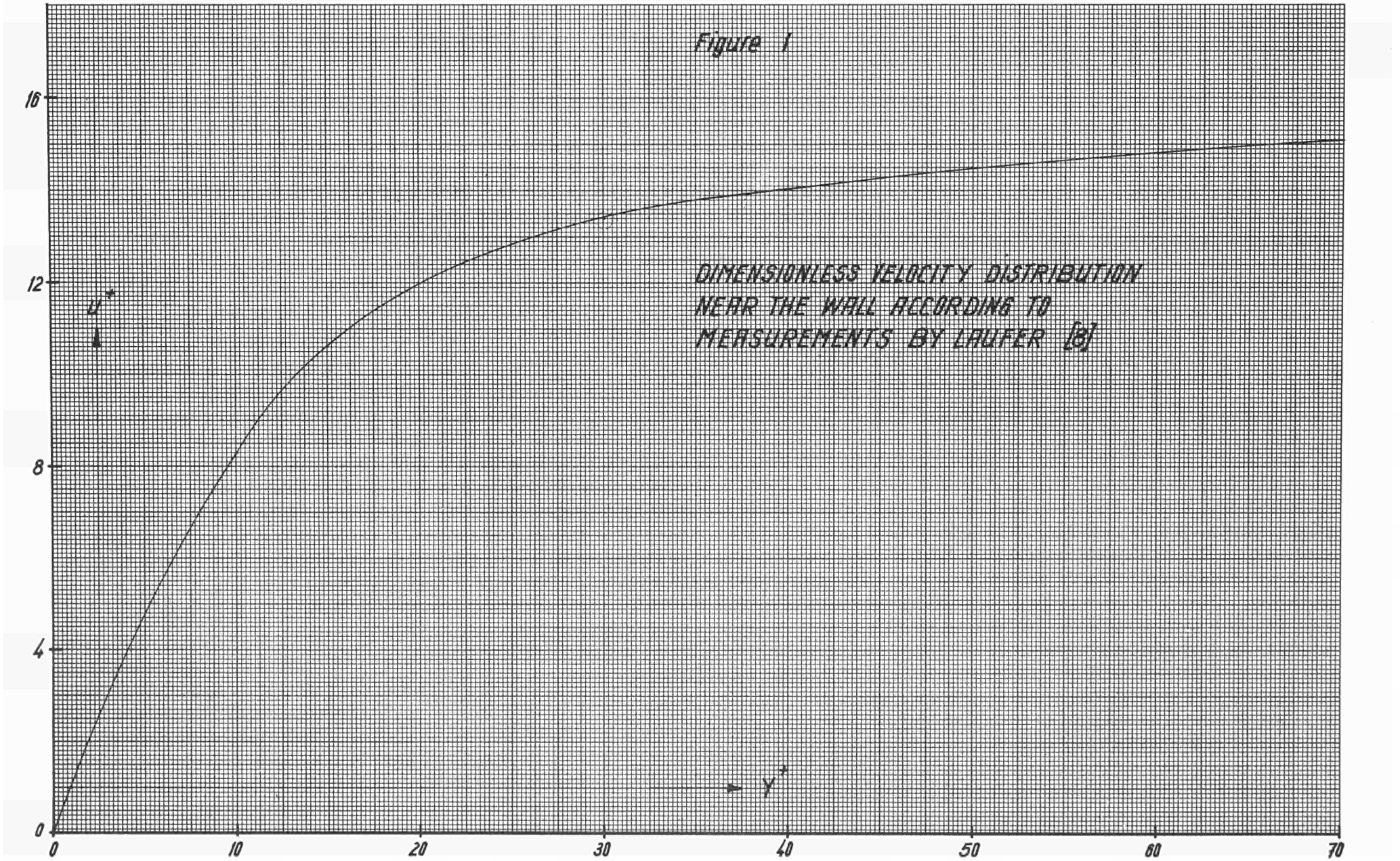


Figure 1
DIMENSIONLESS VELOCITY DISTRIBUTION
NEAR THE WALL ACCORDING TO
MEASUREMENTS BY LAUFER [8]
u*
y*
0
4
8
12
16
0
10
20
30
40
50
60
70

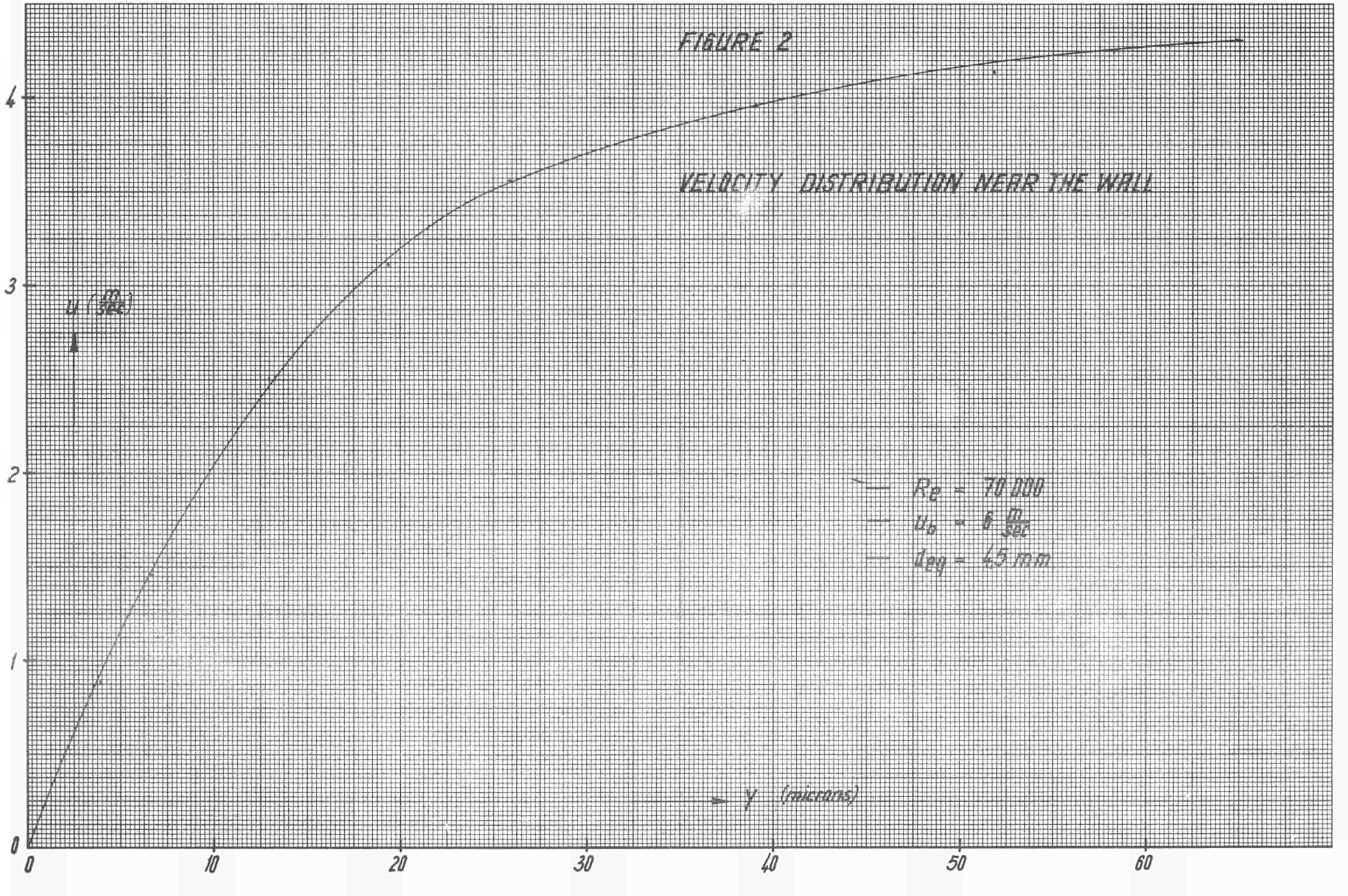


FIGURE 2
VELOCITY DISTRIBUTION NEAR THE WALL
u (ft/sec)
y (microns)
R_e = 70 000
u_b = 6 ft/sec
d_{eq} = 4.5 m.m
0
1
2
3
4
0
10
20
30
40
50
60

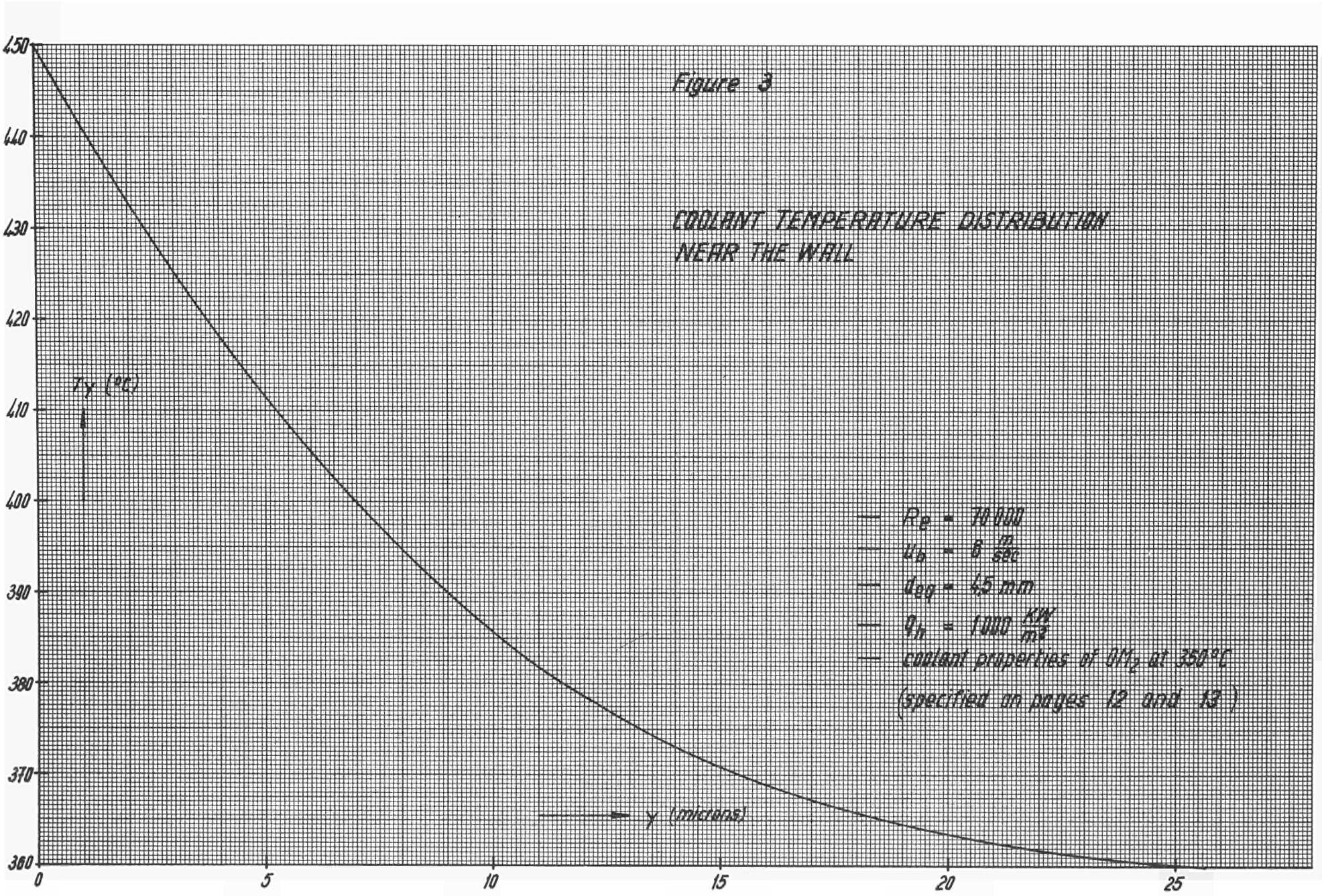


Figure 3
COOLANT TEMPERATURE DISTRIBUTION NEAR THE WALL
T_y (°C)
y (microns)
R_e = 70 000
u_b = 6 m/sec
d_{eq} = 4,5 mm
q_h = 1000 KW/m²
coolant properties of CH_2 at 250°C
(specified on pages 12 and 13)
450
440
430
420
410
400
390
380
370
360
0
5
10
15
20
25

FIGURE 4

SCHEMATIC TEMPERATURE AND CONCENTRATION PROFILES CLOSE TO THE WALL

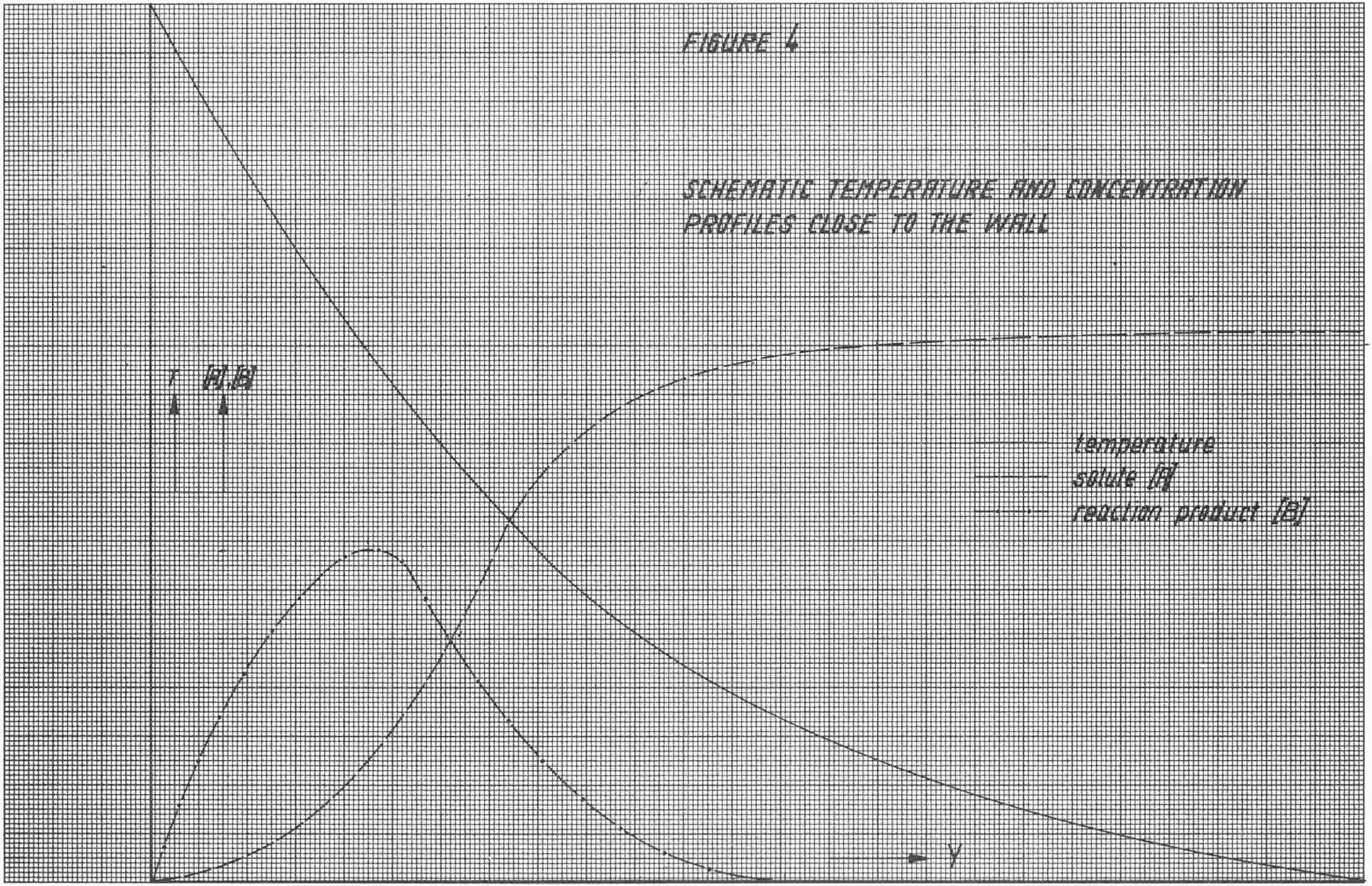
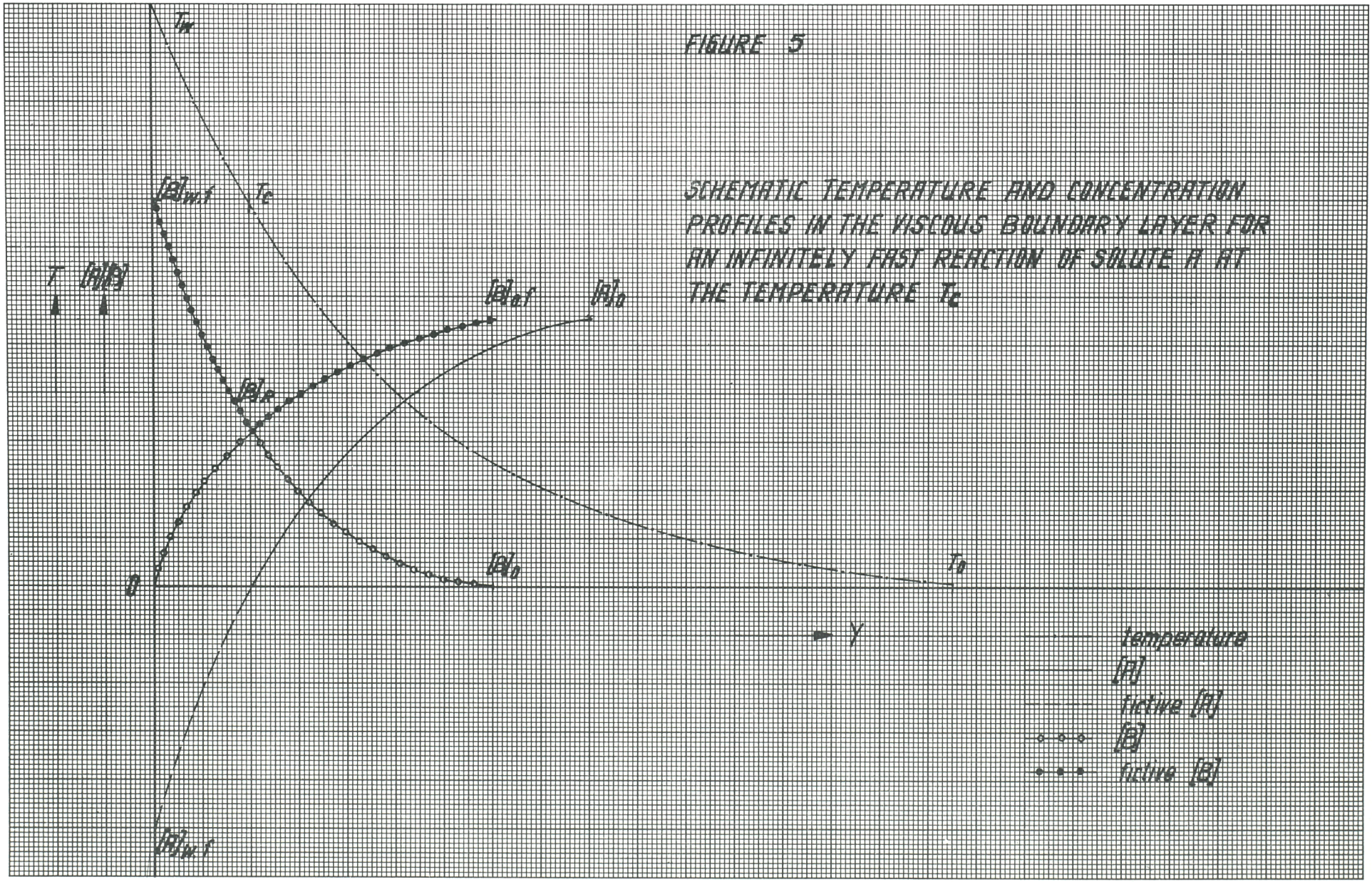


FIGURE 5



SCHEMATIC TEMPERATURE AND CONCENTRATION PROFILES IN THE VISCOUS BOUNDARY LAYER FOR AN INFINITELY FAST REACTION OF SOLUTE A AT THE TEMPERATURE T_c

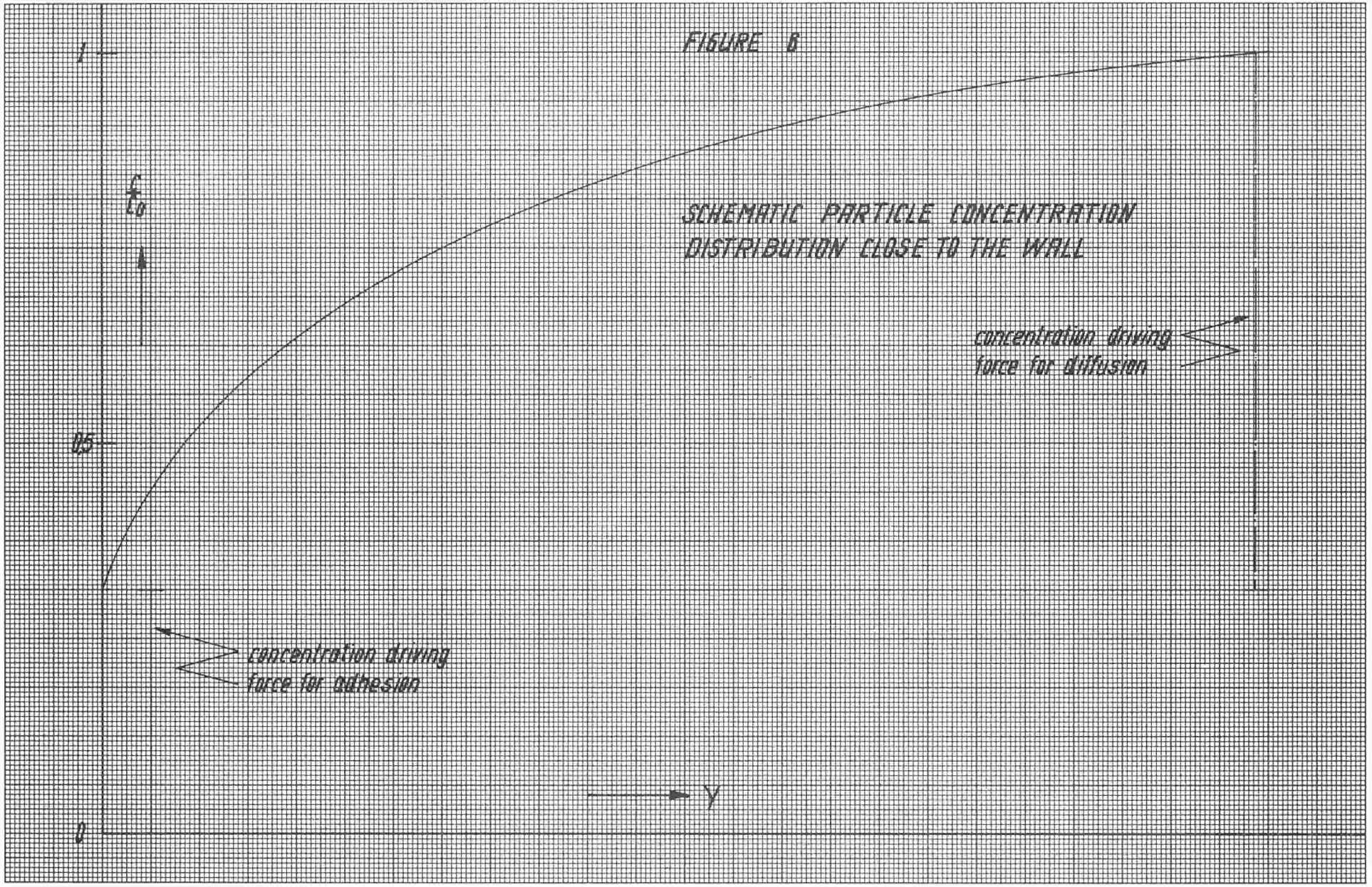
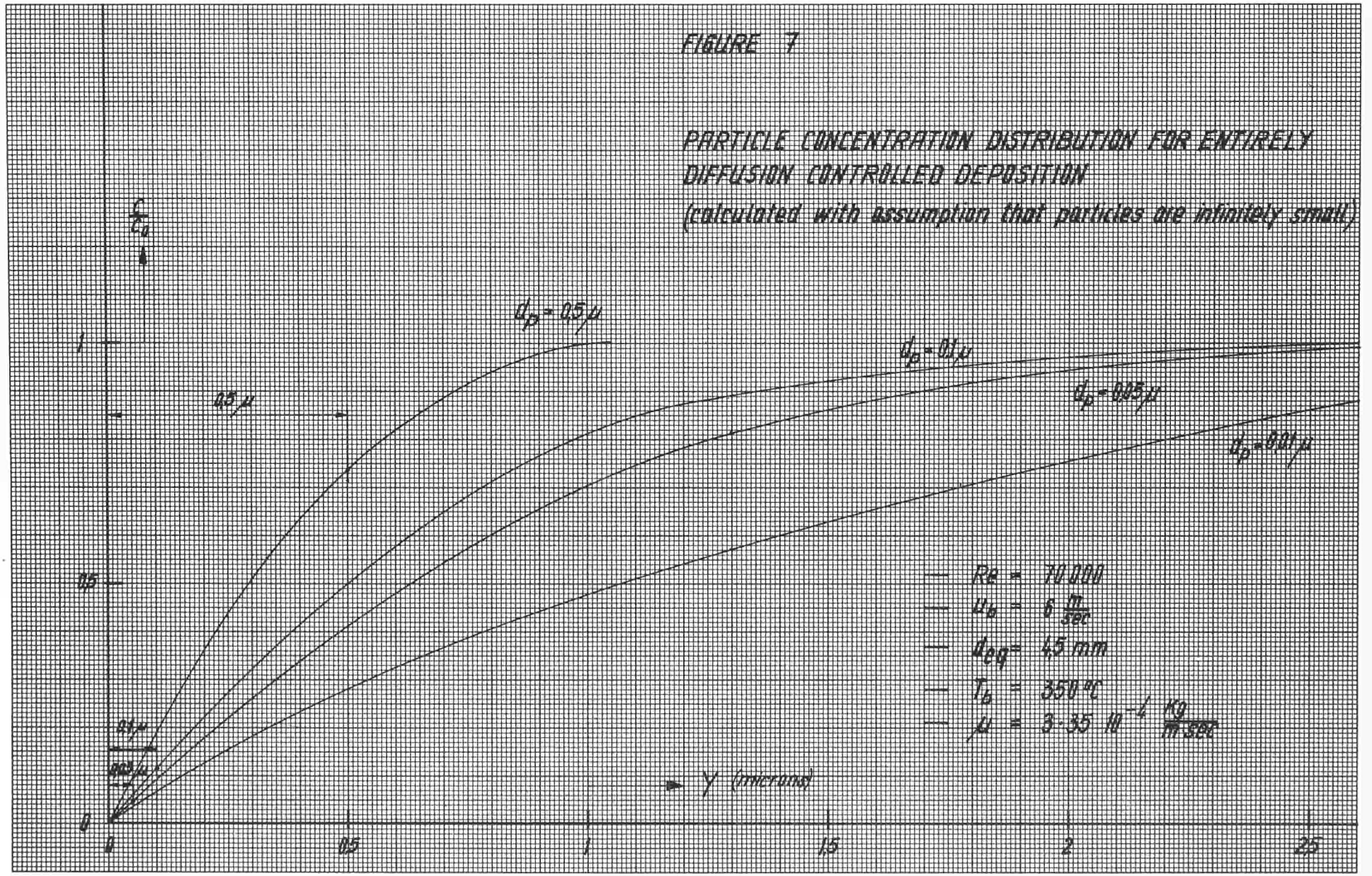


FIGURE 6
SCHEMATIC PARTICLE CONCENTRATION DISTRIBUTION CLOSE TO THE WALL
1
f_0
0.5
0
concentration driving force for adhesion
concentration driving force for diffusion
Y

FIGURE 7

PARTICLE CONCENTRATION DISTRIBUTION FOR ENTIRELY DIFFUSION CONTROLLED DEPOSITION
(calculated with assumption that particles are infinitely small)



LIST OF SYMBOLS

		units
A	flow section	m^2
$[A]$, $[B]$, $[C]$	concentration of compounds A, B, C.	$kmol/m^3$
$[A]_o$, $[B]_o$, $[C]_o$	concentration of compounds A, B, C in the mainstream	$kmol/m^3$
$[A]_w$, $[B]_w$, $[C]_w$	concentration of compounds A, B, C at the wall	$kmol/m^3$
$[A]_{o.f}$, $[B]_{o.f}$	fictive concentration of compounds A, B in the mainstream	$kmol/m^3$
$[A]_{w.f}$, $[B]_{w.f}$	fictive concentration of compounds A, B at the wall	$kmol/m^3$
$[B]_R$	concentration of compound B at the reaction plane	$kmol/m^3$
c	particle concentration	$kg\ m^{-3}$
c_o	particle concentration in the main-stream	$kg\ m^{-3}$
c_w	particle concentration at the wall	$kg\ m^{-3}$
c_p	specific heat	$J\ m^{-3}\ {}^oK^{-1}$
D_A, D_B, D_C	diffusivity of compounds A, B, C	$m^2\ sec^{-1}$
D_p	diffusivity of a particle	$m^2\ sec^{-1}$
d_{eq}	equivalent hydraulic diameter	m
d_p	particle diameter	m
F_{adh}	adhesion force	Newton
F_{dr}	drag force	Newton
f	friction factor	

f_s	friction factor for flow around spherical particle	
k	Boltzmann constant ($1.38\ 10^{-23}$)	J $^oK^{-1}$
k_p	particle adhesion rate constant	m sec^{-1}
$k_{r,t}$	reaction rate constant at temperature T	sec^{-1}
M_A, M_B, M_C	molecular weight of compounds A, B, C	kg
M_s	molecular weight of solvent	kg
m	mass of a particle	kg
n_o	number of particles per unit volume in the mainstream	m^{-3}
n_w	number of particles per unit volume at the wall	m^{-3}
Q_v	volumetric flow rate	m^3 sec^{-1}
q_h	heat flux	J m^{-2} sec^{-1}
q_m	mass transport rate	kg m^{-2} sec^{-1}
q_p	particle deposition rate	kg m^{-2} sec^{-1}
r	distance from pipe centre time	m
t	time	sec
T	temperature	^oK
T_b	bulk coolant temperature	^oC
$T_{b.in}$	bulk coolant temperature at channel inlet	^oC
$T_{b.x}$	bulk coolant temperature at axial position x	^oC
T_o	temperature at the edge of the viscous boundary layer	^oC

T_r	coolant temperature at a distance r from the pipe centre	^oC
T_w	wall temperature	^oC
T_{y^+}	coolant temperature at a dimensionless distance y^+ from the wall	^oC
u	axial coolant velocity	m sec^{-1}
u_a	coolant velocity at wall distance 1/2 d_p	m sec^{-1}
u_b	bulk coolant velocity	m sec^{-1}
u_o	velocity at the edge of the viscous boundary layer	m sec^{-1}
u^+	dimensionless velocity $(u/\sqrt{\frac{\tau_w}{\rho}})$	m sec^{-1}
u_o^+	dimensionless velocity parameter $(u_o/\sqrt{\frac{\tau_w}{\rho}})$	
u_r	velocity at distance r from the pipe centre	m sec^{-1}
u_y	velocity at wall distance y	m sec^{-1}
v	velocity normally to main flow direction and normally to wall	m sec^{-1}
x	coordinate along channel axe (main flow direction)	m
Δx_o	length of elementary viscous boundary layer	m
y	distance from wall in direction normally to wall	m
y^+	dimensionless wall distance $(\frac{y\sqrt{\tau_w/\rho}}{\nu})$	
α	heat transfer coefficient	J m^{-2} sec^{-1} $^oK^{-1}$

δ_h	"hydrodynamic" laminar boundary layer thickness	m
δ_{th}	"thermal" laminar boundary layer thickness	m
δ_m	"diffusion" laminar boundary layer thickness	m
λ	thermal conductivity of coolant	$J\ m^{-1} sec^{-1} {}^oK^{-1}$
μ	dynamic viscosity of coolant	$kg\ m^{-1}\ sec^{-1}$
ν	kinematic viscosity of coolant	$m^2\ sec^{-1}$
ρ	coolant density	$kg\ m^{-3}$
ρ_p	particle density	$kg\ m^{-3}$
τ	shear stress	$N\ m^{-2}$
τ_w	wall shear stress	$N\ m^{-2}$
ϕ_{adh}	rate of particle adhesion at the wall per unit area	$m^{-2}\ sec^{-1}$
ϕ_{coll}	number of particles incident on wall per unit time and per unit area	$m^{-2}\ sec^{-1}$

Dimensionless Groups.

Nu	dimensionless heat transfer coefficient	$(\frac{\alpha d}{\lambda})$
Pr	dimensionless physical property group	$(\frac{\nu}{a})$
Re	dimensionless group characterizing flow conditions	$(\frac{d\ u_b}{\nu})$
Sc	dimensionless physical property group	$(\frac{\nu}{D})$

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